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(71) 出願人 (米国を除くすべての指定国について) 鐘淵化学工業株式会社(KANEKA CORPORATION)[JP/JP] 〒530-8288 大阪府大阪市北区中之島三丁目2番4号 Osaka, (JP)		幸光新太郎(KOMITSU, Shintaro)[JP/JP] 〒676-0074 兵庫県高砂市梅井2丁目3-15 Hyogo, (JP)
(72) 発明者 ; および (75) 発明者／出願人 (米国についてのみ) 中西直明(NAKANISHI, Naoaki)[JP/JP] 〒654-0103 兵庫県神戸市須磨区白川台1丁目27-5-201 Hyogo, (JP) 大内克哉(OUCHI, Katsuya)[JP/JP] 〒655-0046 兵庫県神戸市垂水区舞子台6-6-521 Hyogo, (JP)		(74) 代理人 弁理士 蔦田璋子, 外(TSUTADA, Akiko et al.) 〒541-0048 大阪府大阪市中央区瓦町1丁目7番1号 第百生命大阪瓦町ビル8階 Osaka, (JP)
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(54)Title: HARDENER, CURABLE COMPOSITION AND FOAMABLE RESIN COMPOSITION BOTH CONTAINING THE HARDENER, AND FOAM MADE FROM THE FOAMABLE RESIN COMPOSITION AND PROCESS FOR PRODUCING THE SAME

(54)発明の名称 硬化剤、該硬化剤を用いた硬化性組成物及び発泡性樹脂組成物、及び該発泡性樹脂組成物を用いた発泡体とその製造方法

(57) Abstract

For an organic compound having a carbon-carbon double bond, a hardener having sufficient compatibility therewith is used. A curable composition containing the hardener gives a cured article excellent in mechanical properties and appearance including transparency. A foamable resin composition produced by adding a foaming agent to the curable composition can foam and cure at ordinary temperature or with heating at a relatively low temperature. In particular, even when the foamable resin composition contains a highly polar organic compound having a carbon-carbon double bond, a foam having a high expansion ratio and a high percentage of closed cells can be obtained.

(57)要約

炭素-炭素二重結合を含有する有機系化合物の硬化剤として、該化合物との相溶性が十分な硬化剤を用いる。該硬化剤を用いた硬化性組成物は、機械的特性や透明性等の外観に優れた硬化物を与える。

また、上記硬化性組成物に発泡剤を加えて発泡性樹脂組成物としたとき、常温あるいは比較的低温の加熱下において発泡硬化させることができ、かつ特に極性の高い炭素-炭素二重結合を含有する有機系化合物を用いた場合にも発泡倍率が高く、しかも独立気泡率が高い発泡体を得ることが可能となる。

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## 明細書

硬化剤、該硬化剤を用いた硬化性組成物及び発泡性樹脂組成物、及び該発泡性樹脂組成物を用いた発泡体とその製造方法

## 技術分野

本発明はヒドロシリル基を含有する有機系硬化剤及び該硬化剤を用いた硬化性組成物、及び、常温あるいは比較的低温の加熱下において、発泡、硬化することにより発泡体を生成することを特徴とする発泡性樹脂組成物、その組成物を用いた発泡体、及びその製造方法に関する。

## 背景技術

従来、硬化してゴム状物質を生成する硬化性液状組成物としては、各種のものが開発されている。中でも、深部硬化性に優れた硬化系として、1分子中に平均2個又はそれ以上のビニル基を末端もしくは分子鎖中にもつポリオルガノシロキサンを、珪素原子に結合する水素原子を1分子中に2個以上有するポリオルガノハイドロジエンシロキサンで架橋するものが開発され、その優れた耐候性、耐水性、耐熱性を利用して、シーリング剤、ポッティング剤として使用されている。

しかし、この系はコストが高い、接着性が悪い、カビが発生しやすい等の点からその用途に制限を受けている。更に、上記のポリオルガノシロキサンは一般に有機系重合体に対する相溶性が悪く、ポリオルガノハイドロジエンシロキサンと炭素-炭素二重結合（以下、アルケニル基ともいう）を含有する有機重合体とを硬化させようとしても、相分離によりポリオルガノハイドロジエンシロキサンの加水分解及び

脱水素縮合反応が助長され、ボイド発生のために充分な機械特性が得られないという問題があった。

また、断熱材等の用途に用いられる発泡剤については、重要な特性として熱伝導率が低いことが要求されており、このため、高発泡倍率でしかも高独立気泡率であることが特に望まれている。

上記の問題を解決するため、分子中にヒドロシリル基を有する有機系硬化剤が提案されている（特開平3-95266号公報）。該硬化剤はアルケニル基を含有する有機重合体と一般に相溶性が良好である。ところが、この硬化剤も、例えばフェノール系化合物のような極性の高いアルケニル基を含有する有機系化合物とは十分な相溶性を有さない。そのため、これらの硬化剤と極性の高いアルケニル基を含有する有機系化合物とを硬化させようとしても、相分離により、透明で均一な硬化物が得られ難いという問題があった。

一方、炭素-炭素二重結合を有する有機重合体とヒドロシリル基を有する化合物を主成分として、低毒性で発泡倍率が高い発泡体が得られることが見いだされている（特開平8-815194号公報）。

ところが、上記炭素-炭素二重結合を有する有機重合体とヒドロシリル基を有する化合物から発泡体を得る場合にも、例えばフェノール系化合物のような極性の高い炭素-炭素二重結合を含有する有機系化合物を用いた場合には一般にヒドロシリル基を有する化合物との相溶性が悪く、高発泡倍率で、しかも高独立気泡率である発泡体は得られないという問題があった。

本発明は上記問題に鑑みてなされたものであり、第一の発明は、特に極性の高い炭素-炭素二重結合を含有する有機系化合物とも十分な相溶性を有する硬化剤を提供しようとするものである。

また、第二の発明では、上記した第一の発明に係る硬化剤を用いてなり、透明性が高く均一な硬化物を与える硬化性組成物を提供する。

さらに、第三の発明は、常温あるいは比較的低温の加熱下において発泡硬化させることができ、かつ特に極性の高い炭素-炭素二重結合を含有する有機系化合物を用いた場合にも発泡倍率が高く、しかも独立気泡率が高い発泡体が得られる発泡性樹脂組成物、その組成物を用いた発泡体、及びその製造方法を提供することを目的とする。

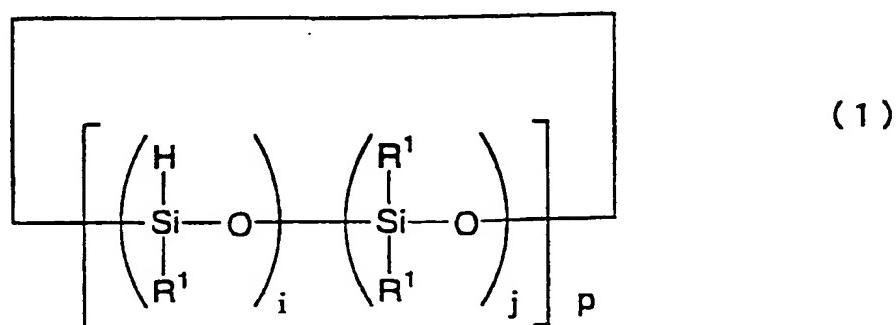
#### 発明の開示

かかる課題を解決するために本発明者らは銳意研究の結果、特定の構造を有する化合物が、分子中に少なくとも1個の炭素-炭素二重結合を有する有機化合物との相溶性が良好なこと、及びこの化合物を硬化剤として用いることにより、上記各課題を解決できることを見出し、本発明に至った。

まず、第一の発明に係る硬化剤は、以下のいずれかの構造を有するものとする。

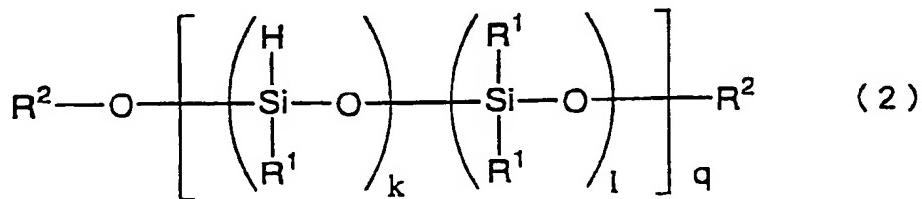
第一の硬化剤は、分子内に1個以上のフェノール性水酸基及び2個以上のヒドロシリル基を有する有機系硬化剤であり、

(a) 下記一般式(1)



(式(1)中、R<sup>1</sup>は、水素原子及び炭素数が1～20の一価の有機基より選ばれる基を表し、それぞれのR<sup>1</sup>は同じであっても異なっていてもよい。i ≥ 2, j ≥ 0, p ≥ 1であり、かつi, j及びpは、3 ≤ (i + j) × p ≤ 50を満足する数である。)

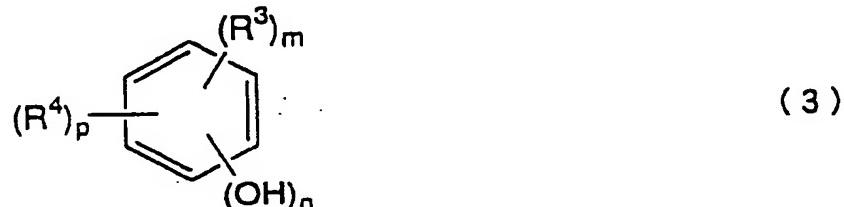
で表される環状オリゴシロキサン、及び／又は下記一般式(2)



(式(2)中、R<sup>1</sup>は上記と同じ、R<sup>2</sup>は、水素原子、-Si(CH<sub>3</sub>)<sub>2</sub>、-Si(CH<sub>3</sub>)<sub>2</sub>H及び炭素数が1～20の一価の有機基より選ばれる基を表し、それぞれのR<sup>2</sup>は同じであっても異なっていてもよい。k ≥ 2, l ≥ 0, q ≥ 1であり、かつk, l及びqは、2 ≤ (k + l) × q ≤ 50を満足する数である。)

で表される鎖状ポリシロキサン、と、

(b) 下記一般式(3)



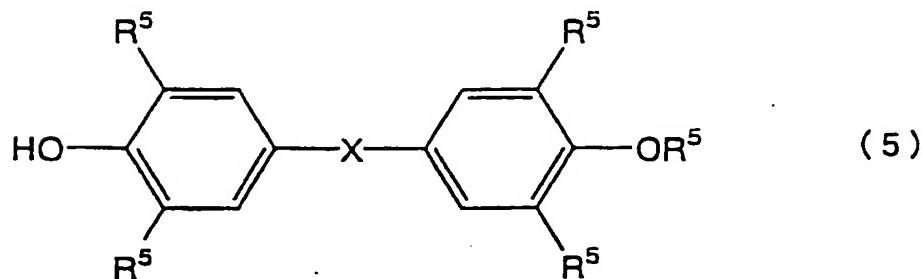
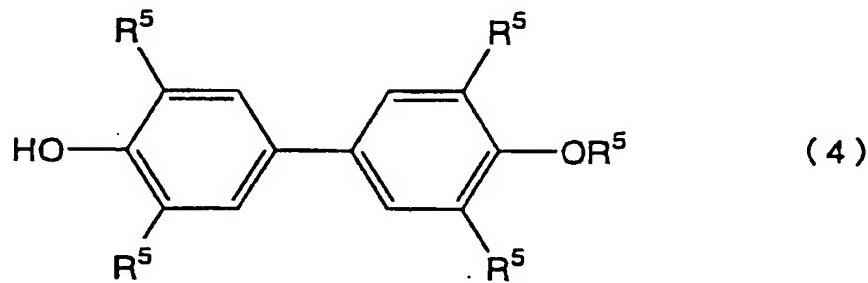
(式(3)中、m及びnは、それぞれ独立に1～3の数を表し、pは0～2の数を表す。R<sup>3</sup>は、1個以上のアルケニル基を含有する炭素数1～25の一価の有機基を表し、mが2以上の場合、それぞれのR<sup>3</sup>は同じであって

も異なっていてもよい。R'は、ハロゲン原子、炭素数1～6のアルコキシ基、炭素数1～25の一価の有機基より選ばれる一価の基を表し、pが2の場合、それぞれのR'は同じであっても異なっていてもよい。)

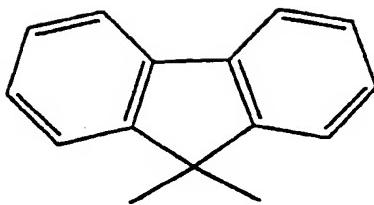
で表される分子内に1個以上のアルケニル基及び1個以上のフェノール性水酸基を有する化合物とを反応させて得られるものである。

上記式(1)及び(2)においては、j及び/又はlが0であるのが好ましい。その場合において、前記iが、 $3 \leq i \leq 7$ を満足する数であり、及び/又は前記kが、 $2 \leq k \leq 10$ を満足する数であるのがより好ましい。

また、(b)成分としては、下記一般式(4)又は一般式(5)



(式(4)及び(5)中、R<sup>5</sup>は、水素原子あるいは1個以上のアルケニル基を含有する炭素数1～10の一価の有機基を表し、それぞれのR<sup>5</sup>は同じであっても異なっていてもよい。式(5)中、Xは、-CH<sub>2</sub>-、-C(C<sub>H</sub><sub>3</sub>)<sub>2</sub>-、-CH(C<sub>H</sub><sub>3</sub>)-、-C(CF<sub>3</sub>)<sub>2</sub>-、-CO-、-SO<sub>2</sub>-、-O-、あるいは次式：



で表される基より選ばれる二価の置換基を示す。)

で表される、分子内に 1 個以上のアルケニル基及び 1 個以上のフェノール性水酸基を有する化合物が特に好適に用いられる。

本発明に係る第二の硬化剤は、次の成分 (i) 、 (ii) 及び (iii) ；

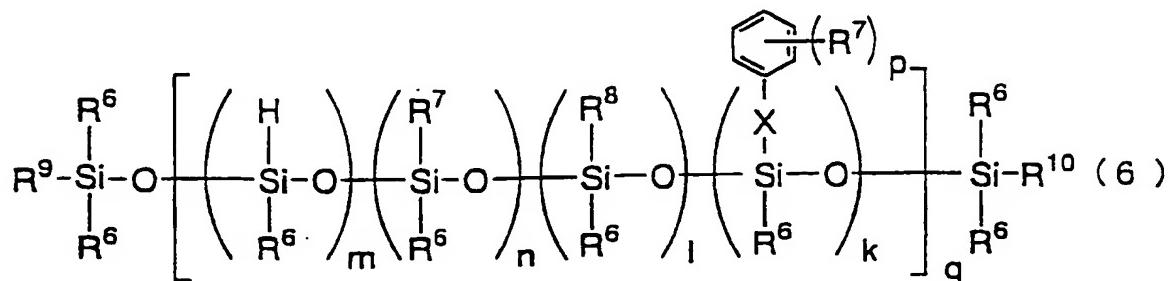
(i) 1 分子中のケイ素原子の数が 3 ~ 10 個である、鎖状及び／又は環状のオルガノハイドロジエンシロキサン、

(ii) (i) 成分のヒドロシリル基と反応しうる官能基を 1 分子中に 2 個以上有する化合物、

(iii) (ii) 成分のヒドロシリル基と反応しうる官能基を 1 分子中に 1 個含有する有機化合物

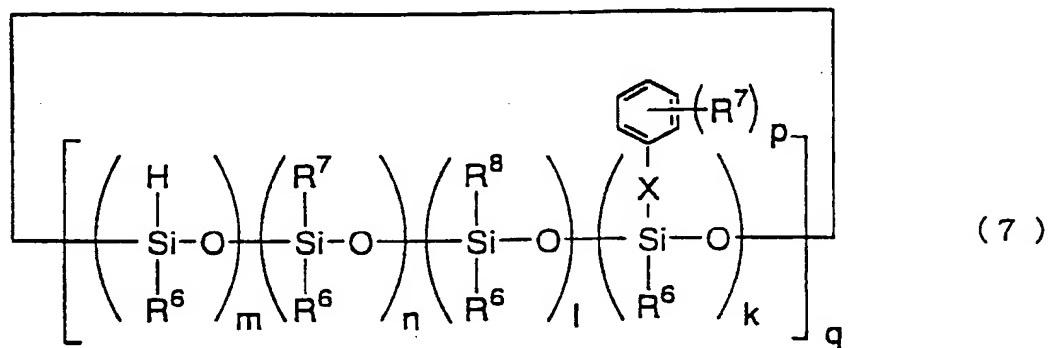
を反応させて得られ、しかも (i) 成分由来のヒドロシリル基が実質上残存した化合物である。

また、第三の硬化剤は、次の式 (6) 又は式 (7) で示される構造を有することを特徴とする。



(式 (6) 中、  $m \geq 2$  、  $n \geq 0$  、  $l$  、  $k$  、  $q \geq 1$  、  $p$  は 0 ~ 5 の整数、  $10 \leq (m + n + l + k) \times q \leq 80$  であり、  $R^6$  、  $R^7$  は、炭素数 0 ~ 6 の

1価の置換基、 $R^8$ は、分子量が100～10,000のポリオキシアルキレン鎖を示し、 $R^9$ 、 $R^{10}$ は、水素又は炭素数1～20の炭化水素基を示す。m個、n個、1個、k個の $R^6$ 、n個、p個の $R^7$ は、それぞれ同じものでも異なるものでもよい。Xは、構成元素としてC、H、N、O、S、ハロゲンのみを含む炭素数0～10の2価の置換基を示す。)



(式(7)中、 $m \geq 2$ 、 $n \geq 0$ 、 $l$ 、 $k$ 、 $q \geq 1$ 、 $p$ は0～5の整数、 $3 \leq (m+n+l+k) \times q \leq 20$ であり、 $R^6$ 、 $R^7$ 、 $R^8$ 、Xは、式(6)と同じ。)

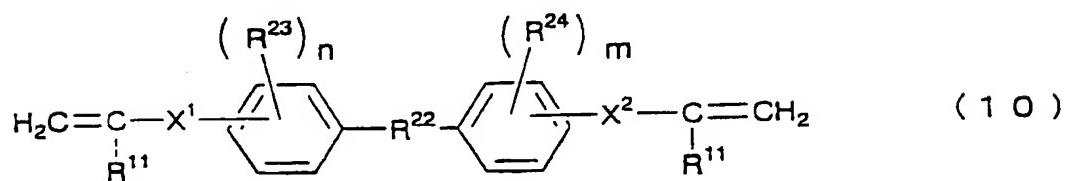
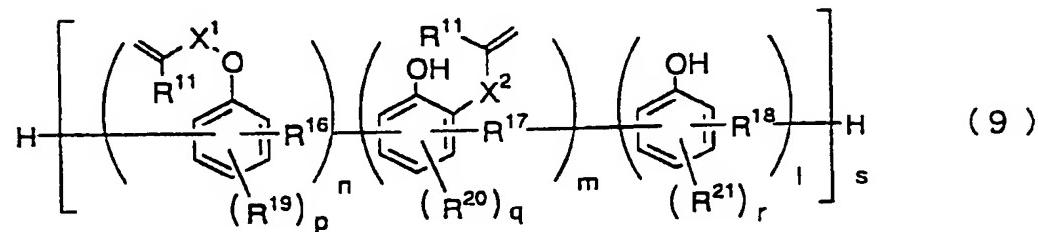
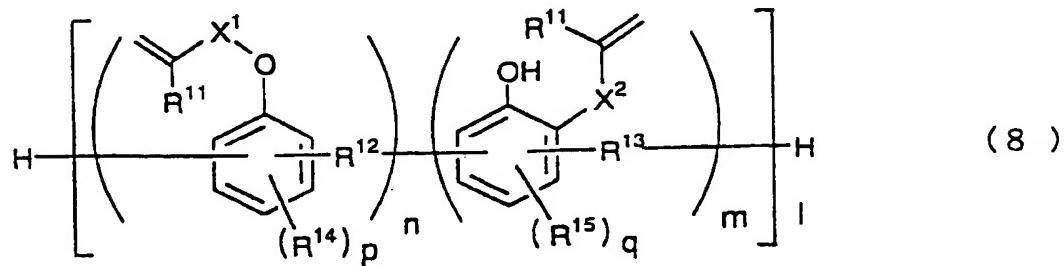
次に、第二の発明に係る硬化性組成物は、(A)分子中に少なくとも1個の炭素-炭素二重結合を含有する有機化合物と、(B)ヒドロシリル基を有する有機系硬化剤とを必須成分として含有し、好ましくは、(C)ヒドロシリル化触媒をさらに含有し、その(B)成分として、上記第一の発明の有機系硬化剤のいずれか1種又は2種以上を含有するものである。

第三の発明に係る発泡性樹脂組成物は、上記(A)成分及び(B)成分に加えて(D)発泡剤及び/又はOH基を有する化合物をさらに必須成分として含有し、好ましくは(C)ヒドロシリル化触媒をさらに含有するものである。

第二及び第三の発明における(A)成分の有機化合物の分子骨格は、炭

素、酸素、水素、窒素、イオウ、ハロゲンのうちのいずれか1種以上の元素のみからなるのが好ましい。

より具体的には、(A) 成分の有機化合物としては、下記一般式(8)～式(10)



(式(8)～式(10)において、R<sup>11</sup>は、H又はCH<sub>3</sub>を示し、R<sup>12</sup>、R<sup>13</sup>、R<sup>16</sup>、R<sup>17</sup>、R<sup>18</sup>、R<sup>22</sup>は、炭素数0～6の2価の置換基を示し、R<sup>14</sup>、R<sup>15</sup>、R<sup>19</sup>、R<sup>20</sup>、R<sup>21</sup>、R<sup>23</sup>、R<sup>24</sup>は、炭素数0～6の1価の置換基を示し、X<sup>1</sup>、X<sup>2</sup>は、炭素数0～10の2価の置換基を示す。また、式(8)において、n、mは、0～300の整数、lは、1～300の整数、p、qは、0～3の整数を示し、式(9)において、n、m、lは、0～300の整数、

s は、1～300 の整数、p, q, r は、0～3 の整数を示し、式(10)において、n, m は、0～4 の整数を示す。)

のうちのいずれか 1 種以上の構造を分子骨格として有するものが好適に用いられる。

上記(A) 成分の有機化合物の炭素－炭素二重結合は、1 分子あたり平均 2 個以上であるのが好ましい。

上記(D) 成分の発泡剤の例としては、炭化水素、エーテル類、ハイドロクロロフルオロカーボン、又はハイドロフルオロカーボンから選ばれる化合物、あるいはそれらの混合物が挙げられる。また、OH 基を有する化合物の例としては、アルコール、カルボン酸、及び水のうちの 1 種以上が挙げられる。

上記発泡性樹脂組成物を常温あるいは比較的低温の加熱下において発泡硬化させることにより、発泡倍率が高く、しかも独立気泡率が高い発泡体が得られる。

#### 発明を実施するための最良の形態

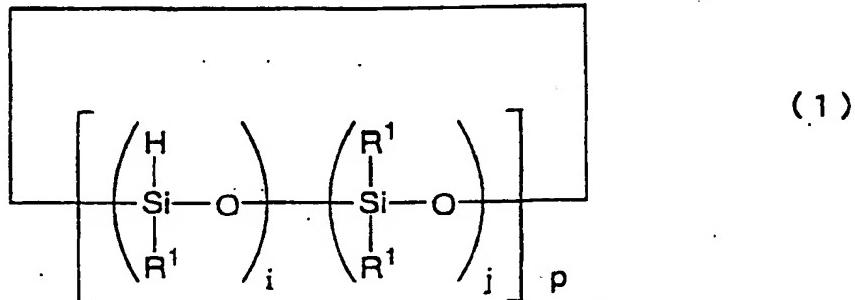
上記第一～第三の発明を以下、詳細に説明する。

##### 1. 硬化剤

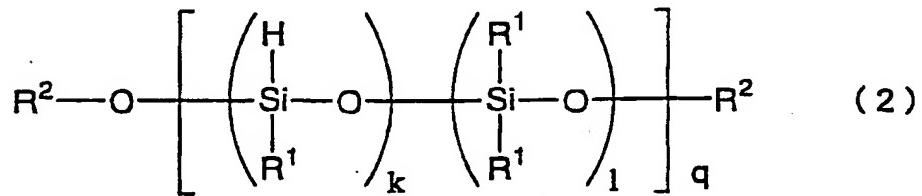
第一の発明に係る硬化剤は、分子中に少なくとも 1 個の炭素－炭素二重結合を含有する有機化合物との相溶性が良好なことを特徴とする。ここで、「有機化合物」とは、分子骨格中に実質的にシロキサン結合を含まない化合物をいい、「相溶性が良好」とは、上記有機化合物と混合攪拌した際に均一状態に溶解し、肉眼による観察で白濁や相分離が認められないことをいうものとする。もしくは、混合攪拌後、1000 回転／分で 10 分間程度遠心分離しても白濁や相分離が認められないことをいうものとする。

相溶性が良好であることにより、これを用いて得られる硬化物は機械的特性及び透明性等の外観に優れたものとなり、また発泡体は独立気泡率が高く、その結果断熱性能等に優れたものとなる。

その具体的な構造として、第一の硬化剤は、(a) 下記一般式 (1)



で表される環状オリゴシロキサン及び／又は下記一般式 (2)



で表される鎖状ポリシロキサンと、

(b) 下記一般式 (3)



(式 (3) 中、m及びnは、それぞれ独立に1～3の数を表し、pは0～2の数を表す。R³は、1個以上のアルケニル基を含有する炭素数1～25の一価の有機基を表し、mが2以上の場合、それぞれのR³は同じであっても異なっていてもよい。R⁴は、ハロゲン原子、炭素数1～6のアルコキシ基、炭素数1～25の一価の有機基より選ばれる一価の基を表し、pが2

の場合、それぞれの R' は同じであっても異なっていてもよい。) で表される分子内に 1 個以上のアルケニル基及び 1 個以上のフェノール性水酸基を有する化合物とを反応させて得られる化合物である。

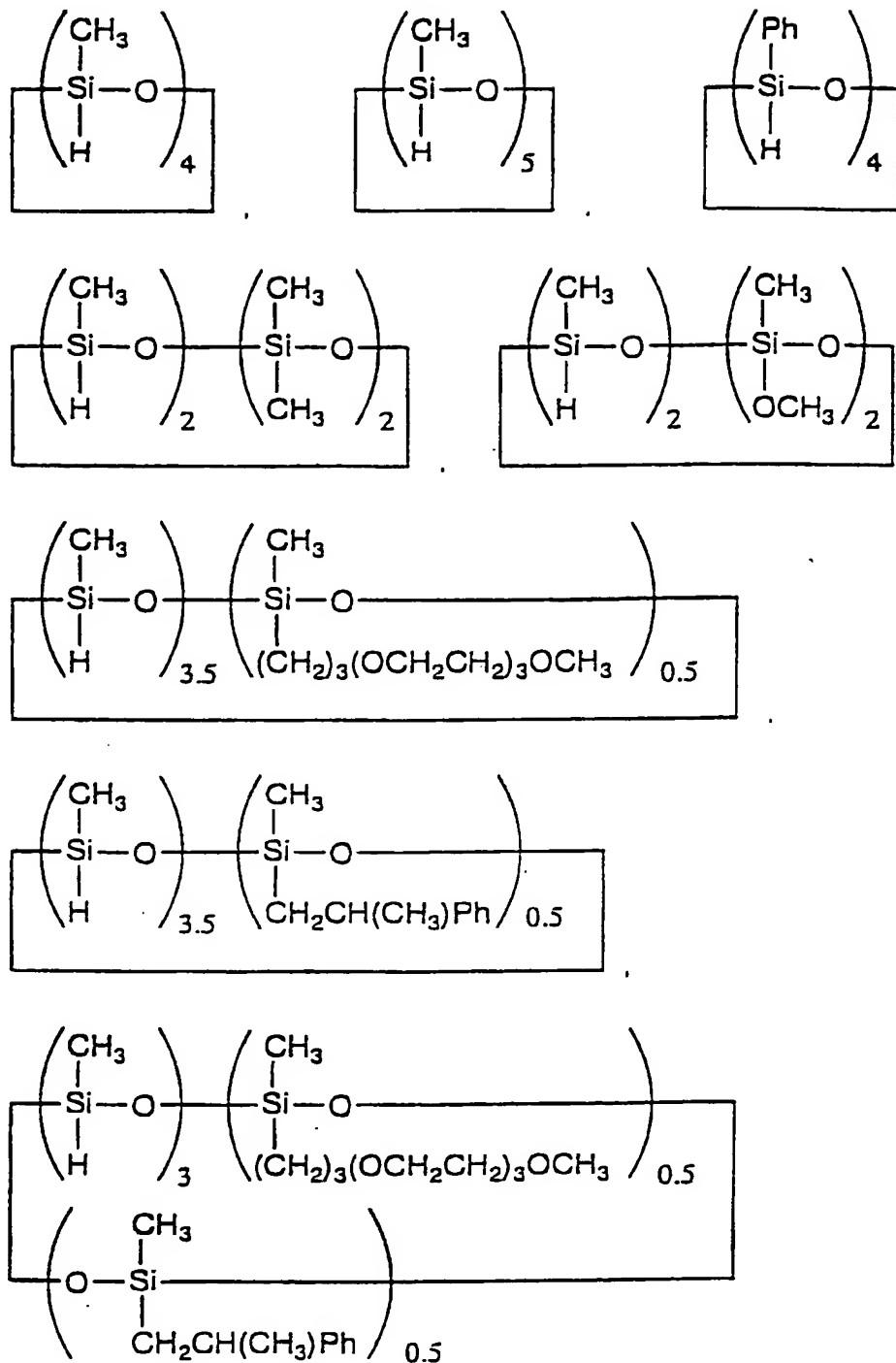
上記一般式 (1) で表される環状ポリシロキサン及び一般式 (2) で表される鎖状ポリシロキサンの R' は、水素原及び炭素数が 1 ~ 20 の一価の有機基より選ばれる基であり、一価の有機基の例としてはアルコキシ基、ハロゲン化アルキル基、アルキル基、シクロアルキル基、アルケニル基、シクロアルケニル基、あるいはアリール基等が挙げられる。これらのうち、トリフルオロプロピル基、メチル基、エチル基、 $-CH_2CH_2R$  で表される置換アルキル基 (ここでいう R は、ハロゲン原子、シアノ基、フェニル基、アルコキシ基、アルキルカルボニル基、アルコキシカルボニル基等の一価の有機基を表す。)、 $-CH_2CH(CH_3)R$  で表される置換アルキル基 (ここでいう R は、ハロゲン原子、フェニル基、アルキルカルボニル基、アルコキシカルボニル基等の一価の有機基を表す。)、 $-CH_2CH_2CH_2R$  で表される置換アルキル基 (ここでいう R は、ハロゲン原子、水酸基、アルコキシ基等の一価の有機基を表す。)、フェニル基が工業的に一般に入手容易なこと、及び化学的安定性の点から好ましい。これらのうち、メチル基、トリフルオロプロピル基、フェニル基、2-フェニルエチル基、あるいは $-CH_2CH_2CH_2(OCH_2CH_2)_nOCH_3$  (ここでいう n は、0 又は 2 以下の正の数を表す。) で表される置換アルキル基がさらに好ましく、最も好ましいのはメチル基である。なお、それぞれの R は同一であっても異なっていてもよい。

前記一般式 (2) で表される鎖状ポリシロキサンの R' は、水素原子、 $-Si(CH_3)_3$ 、 $-Si(CH_3)_2H$ 、及び炭素数が 1 ~ 20 の一価の有機基より選ばれる基であり、一価の有機基の例としては、メチル基、エチル

基、プロピル基、ブチル基、フェニル基、あるいは $-(CH_2CH_2O)_nCH_2$ （ここでいうnは0又は20以下の正の数を表す）で表される置換アルキル基が挙げられる。

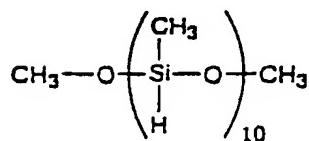
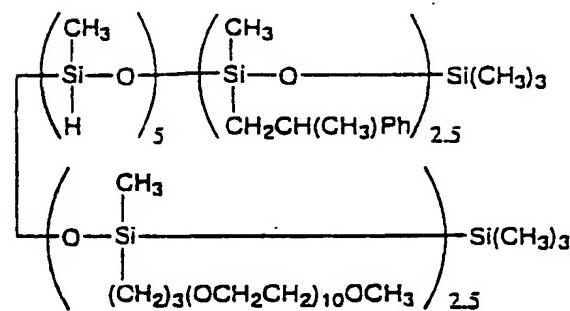
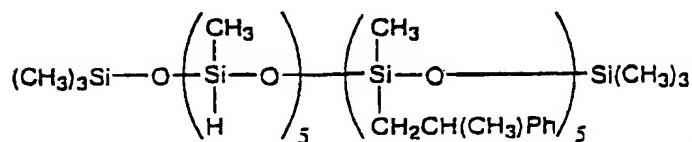
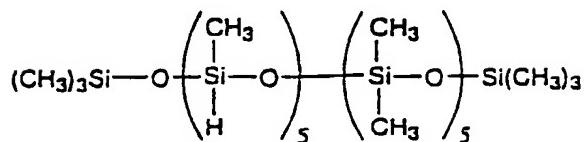
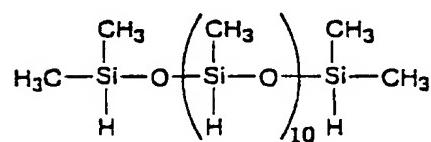
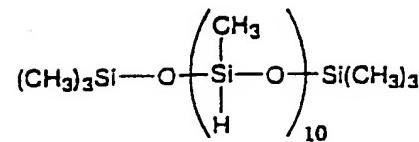
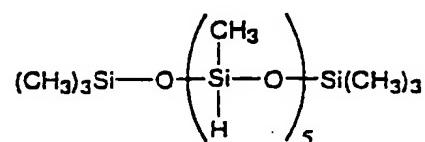
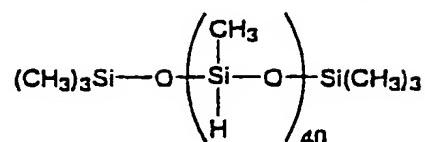
前記一般式（1）で表される環状ポリシロキサンのi、j、p、及び前記一般式（2）で表される鎖状ポリシロキサンのk、l、qのうち、iは2以上の数、jは0又は正の数、pは1以上の数であり、かつi、j及びpは $3 \leq (i+j) \times p \leq 50$ を満足する数であり、kは2以上の数、lは0又は正の数、qは1以上の数であり、かつk及びlは $2 \leq (k+l) \times q \leq 50$ を満足する数であればよいが、工業的に一般に入手が容易である点からj=1=0であることが好ましい。さらに、得られる硬化剤が低粘度で取り扱い性がよい等の点から、 $3 \leq i \leq 7$ 及び／又は $2 \leq k \leq 10$ であることが好ましい。

前記一般式（1）で表される環状ポリシロキサンの具体例としては、次式：



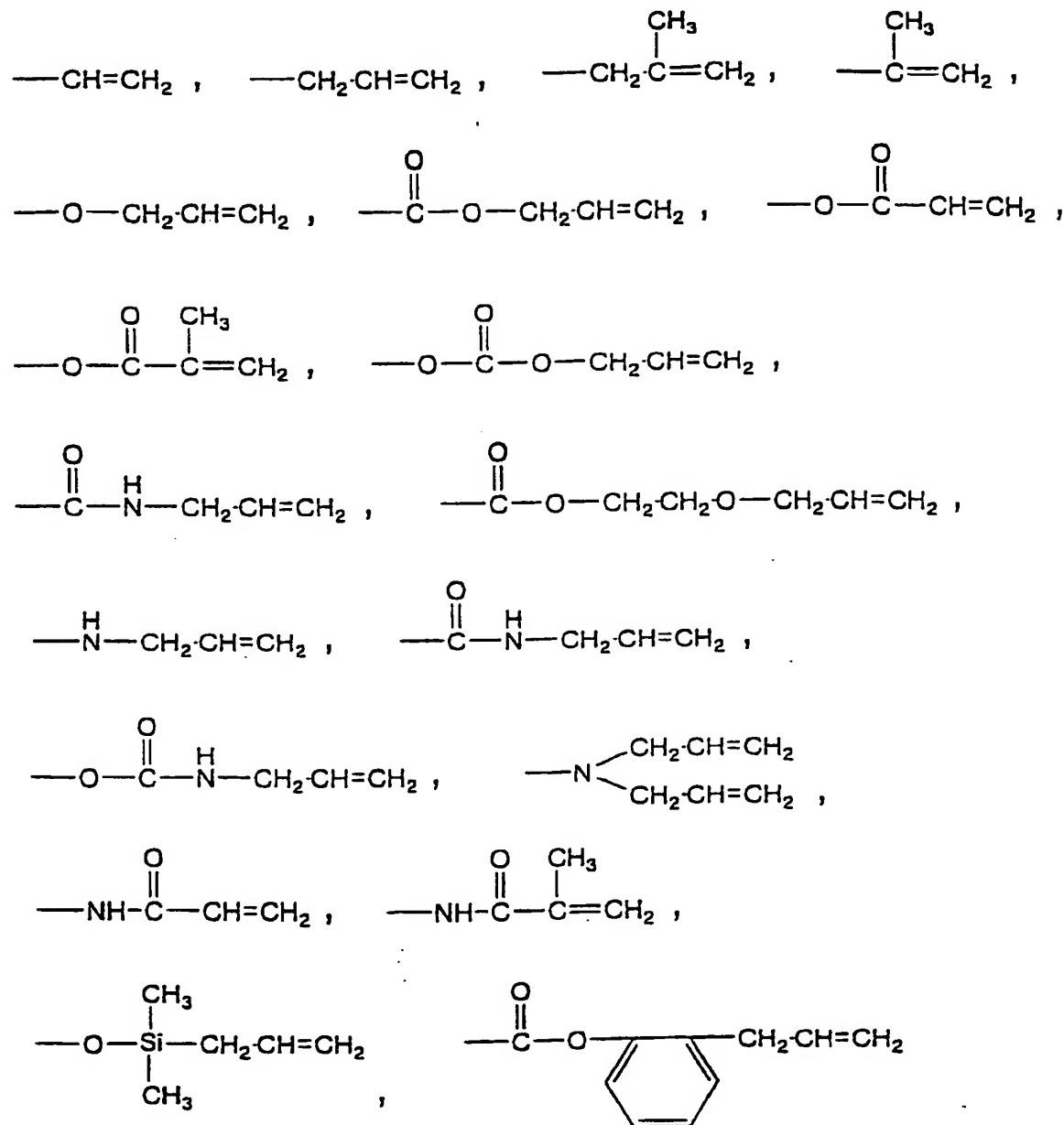
で表される化合物が挙げられる。

前記一般式（2）で表される鎖状ポリシロキサンの具体例としては、式



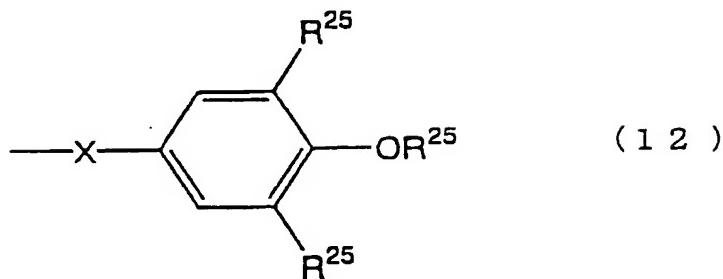
で表される化合物が挙げられる。

前記一般式(3)で表される分子内に1個以上のアルケニル基及び1個以上のフェノール性水酸基を有する化合物のR<sup>3</sup>の例としては、式

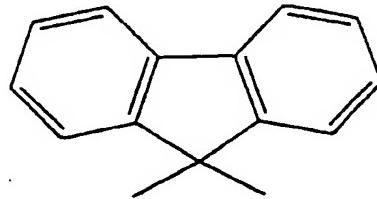


で表される基が挙げられる。

あるいは下記一般式 (11) 又は (12)



(式 (11) 及び (12) 中、R<sup>25</sup>は水素原子あるいはアリル基であり、かつ少なくとも一つのR<sup>25</sup>はアリル基である。式 (12) 中、Xは、-C H<sub>2</sub>-、-C (CH<sub>3</sub>)<sub>2</sub>-、-CH (CH<sub>3</sub>) -、-C (CF<sub>3</sub>)<sub>2</sub>-、-CO-、-SO<sub>2</sub>-、-O-、あるいは式：



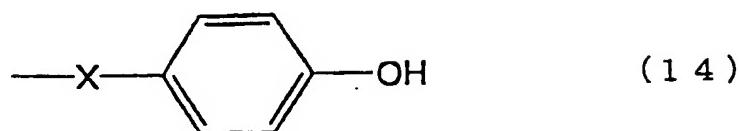
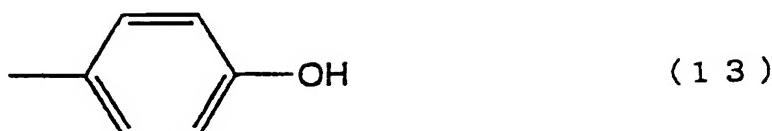
で表される基である。)

で表される基が挙げられる。

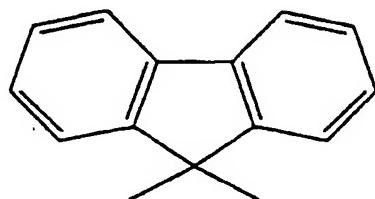
これらのうち、アリル基あるいは上記一般式 (11) 又は (12) で表される基が、工業的に一般に入手可能なこと、あるいはヒドロシリル基との反応性が良好なことから好ましい。

上記一般式 (3) で表される分子内に 1 個以上のアルケニル基及び 1 個以上のフェノール性水酸基を有する化合物のR<sup>4</sup>の例としては、塩素原子、

メトキシ基、メチル基、ヒドロキシカルボニル基、アルコキシカルボニル基、あるいは下記一般式(13)又は(14)



(式(14)中、Xは、 $-CH_2-$ 、 $-C(CH_3)_2-$ 、 $-CH(CH_3)-$ 、  
 $-C(CF_3)_2-$ 、 $-CO-$ 、 $-SO_2-$ 、 $-O-$ 、あるいは式：

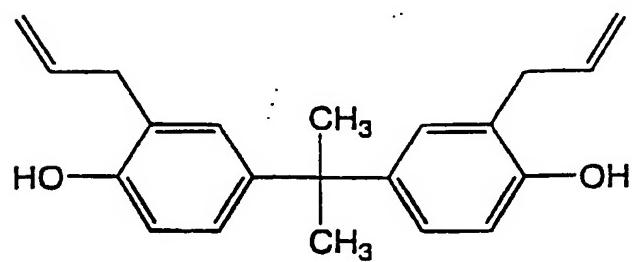
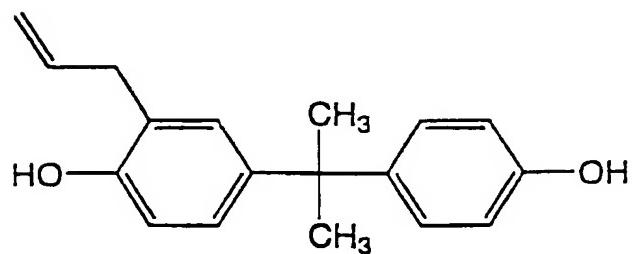
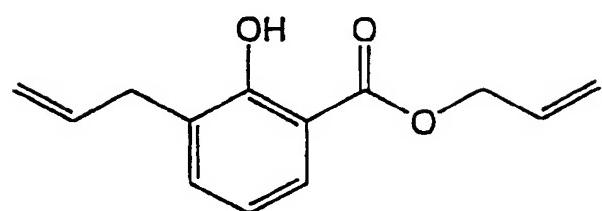
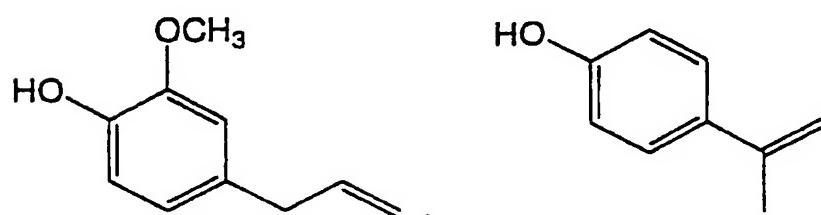
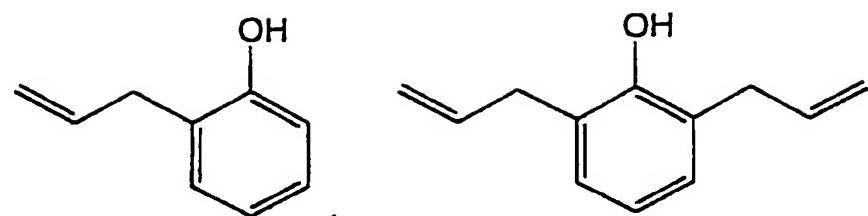


で表される基を示す。)

で表される基が挙げられる。

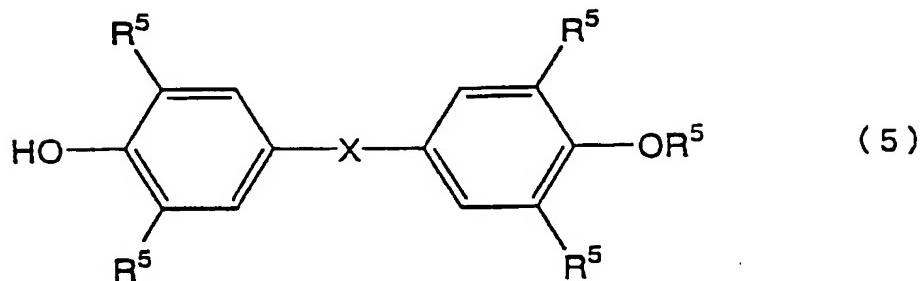
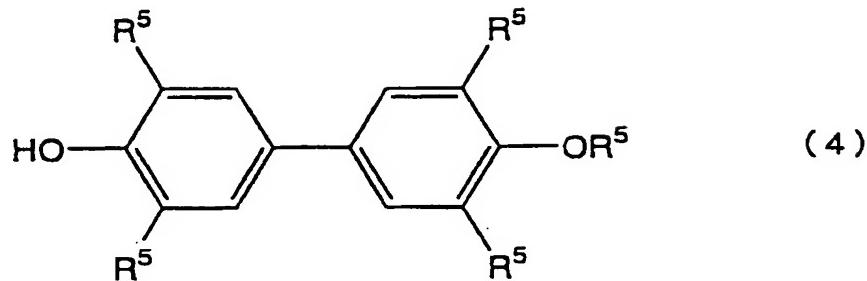
これらのうちメトキシ基、あるいは上記一般式(13)又は(14)で表される基が、工業的に一般に入手可能なことから好ましい。これらの置換基が2個以上置換している場合はそれぞれ同一であっても異なっていてもよい。

上記一般式(3)で表される分子内に1個以上のアルケニル基及び1個以上のフェノール性水酸基を有する化合物の具体例としては、式：

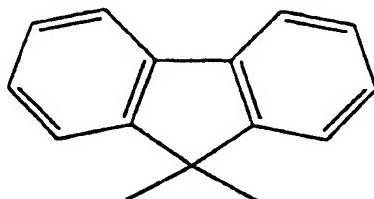


で表される化合物が挙げられる。

以上（b）成分について述べたが、中でも、下記一般式（4）又は（5）



（式（4）及び（5）中、R<sup>5</sup>は、水素原子あるいは1個以上のアルケニル基を含有する炭素数1～10の一価の有機基を表し、それぞれのR<sup>5</sup>は同じであっても異なっていてもよい。Xは、-CH<sub>2</sub>-、-C(CH<sub>3</sub>)<sub>2</sub>-、-CH(CH<sub>3</sub>)-、-C(CF<sub>3</sub>)<sub>2</sub>-、-CO-、-SO<sub>2</sub>-、-O-、あるいは式：



で表される基より選ばれる二価の置換基を示す。）

で表される、分子内に1個以上のアルケニル基及び1個以上のフェノール性水酸基を有する化合物が好適に用いられる。

本発明の硬化剤は、上記（a）成分と（b）成分とを反応させて得ることができるが、その際用いられるヒドロシリル化触媒の具体例としては、

白金の単体、アルミナ、シリカ、カーボンブラック等の担体に固体白金を担持させたもの、塩化白金酸、塩化白金酸とアルコール、アルデヒド、ケトン等との錯体、白金-オレフィン錯体（例えば、Pt( $\text{CH}_2=\text{CH}_2$ )<sub>n</sub>( $\text{PPh}_3$ )<sub>2</sub>、Pt( $\text{CH}_2=\text{CH}_2$ )<sub>n</sub> $\text{C}_{12}$ ）、白金-ビニルシロキサン錯体（例えば、Pt( $\text{ViMe}_2\text{SiOSiMe}_2\text{Vi}$ )<sub>n</sub>、Pt[( $\text{MeViSiO}$ )<sub>4</sub>]<sub>n</sub>）、白金-ホスフィン錯体（例えば、Pt( $\text{PPh}_3$ )<sub>4</sub>、Pt( $\text{PBu}_3$ )<sub>4</sub>）、白金-ホスファイト錯体（例えば、Pt[P(OPh)<sub>3</sub>]<sub>n</sub>、Pt[P(OBu)<sub>3</sub>]<sub>n</sub>）（式中、Meはメチル基、Buはブチル基、Viはビニル基、Phはフェニル基を表わし、n、mは整数を表わす。）、ジカルボニルジクロロ白金、カールシュテト（Karstedt）触媒、また、アシュビー（Ashby）の米国特許第3,159,601号及び第3,159,662号明細書中に記載された白金-炭化水素複合体、ならびにラモロー（Lamoreaux）の米国特許第3,220,972号明細書中に記載された白金アルコラート触媒が挙げられる。さらに、モディック（Modic）の米国特許第3,516,946号明細書中に記載された塩化白金-オレフィン複合体も本発明において有用である。また、白金化合物以外の触媒の例としては、RhCl( $\text{PPh}_3$ )<sub>3</sub>、RhCl<sub>3</sub>、Rh/Al<sub>2</sub>O<sub>3</sub>、RuCl<sub>3</sub>、IrCl<sub>3</sub>、FeCl<sub>3</sub>、AlCl<sub>3</sub>、PdCl<sub>2</sub>·2H<sub>2</sub>O、NiCl<sub>2</sub>、TiCl<sub>4</sub>等が挙げられる。これらの中では、触媒活性の点から塩化白金酸、白金-オレフィン錯体、白金-ビニルシロキサン錯体等が好ましい。また、これらの触媒は単独で使用してもよく、2種以上併用してもよい。

触媒の添加量は特に限定されないが、ヒドロシリル基1モルに対して、 $10^{-1} \sim 10^{-3}$ モルの範囲が好ましく、より好ましくは、 $10^{-2} \sim 10^{-6}$ モルの範囲である。

上記の触媒と共に助触媒としてホスフィン系化合物及びホスフィン錯体

を使用することができる。そのようなホスフィン系化合物としては、トリフェニルホスフィン、 $\text{PMe}_3$ 、 $\text{PET}_3$ 、 $\text{PPr}_3$ （ここで、 $\text{Pr}$ はプロピル基を表す。以下同様。）、 $\text{P}(n-\text{Bu})_3$ 、 $\text{P}(\text{cyclo}-\text{C}_5\text{H}_{11})_3$ 、 $\text{P}(p-\text{C}_6\text{H}_4\text{Me})_3$ 、 $\text{P}(o-\text{C}_6\text{H}_4\text{Me})_3$ 等があるがこれらに限定されるものではない。ホスフィン錯体としては、例えば、 $\text{Cr}(\text{CO})_3\text{PPh}_3$ 、 $\text{Cr}(\text{CO})_4(\text{PPh}_3)_2$ （シス及びトランス異性体）、 $\text{Cr}(\text{CO})_3(\text{PPh}_3)_2$ （fac及びmer異性体）、これらCr化合物のMo及びV類縁体、 $\text{Fe}(\text{CO})_4\text{PPh}_3$ 、 $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ 、ならびにこれらFe化合物のRu及びOs類縁体、 $\text{CoCl}_2(\text{PPh}_3)$ 、 $\text{RhCl}(\text{PPh}_3)_3$ 、 $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ 、 $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ 、 $\text{NiCl}_2(\text{PPh}_3)_2$ 、 $\text{PdCl}_2(\text{PPh}_3)_2$ 、 $\text{PtCl}_2(\text{PPh}_3)_2$ 、及び $\text{ClAu}(\text{PPh}_3)$ がある。さらに、トリフェニルホスフィン以外のホスフィンを含有する上記の金属の錯体等のような金属錯体も有効な助触媒となりうる。さらに、 $\text{P}(\text{OPh})_3$ 等のようなホスファイト、 $\text{AsPh}_3$ 等のようなアルシン及び $\text{SbPh}_3$ 等のようなスチビンを含有する錯体も有効な助触媒となりうる。

助触媒の添加量は特に限定されないが、触媒1モルに対して、 $10^{-2} \sim 10^2$ モルの範囲が好ましく、より好ましくは $10^{-1} \sim 10^1$ モルの範囲である。

ヒドロシリル化反応においては、溶剤の使用は特に必要とされないが、始発原料等が固体あるいは高粘度のものであって、攪拌等の操作に困難をともなう場合には適宜不活性有機溶剤を使用することは差し支えなく、これにはベンゼン、トルエン、キシレン等の芳香族炭化水素系溶剤、ヘキサン、オクタン等の脂肪族炭化水素系溶剤、エチルエーテル、ブチルエーテル、テトラヒドロフラン等のエーテル系溶剤、メチルエチルケトン等のケ

トン系溶剤、クロロホルム、塩化メチレン、トリクロロエチレン等のハロゲン化炭化水素系溶剤、酢酸エチル等のエステル系溶剤等が例示される。用いる溶剤の量は、特に限定されないが、経済性の点から用いる反応剤の総量100重量部に対して100重量部以下が好ましく用いられる。

本発明に使用される(a)、(b)両成分及びヒドロシリル化触媒の添加方法については、3成分を一括して仕込む方法、(b)成分に(a)成分とヒドロシリル化触媒とを添加する方法、(a)成分及びヒドロシリル化触媒に(b)成分を添加する方法、(a)成分を(b)成分及び触媒へ添加する方法、各成分を同時に添加する方法等が考えられるが、特に制限はない。

しかし、ヒドロシリル基が反応後も残存するように反応させるためには、(a)成分である多価ハイドロジエンシリコン化合物が(b)成分に対し常に過剰に存在することが望ましいと考えられるので、(b)成分であるアルケニル基を含有する有機化合物とヒドロシリル化触媒を混合したものを、(a)成分である多価ハイドロジエンシリコン化合物に添加する方法が好ましい。

(a)成分と(b)成分との混合比は、ヒドロシリル基とアルケニル基のモル比でヒドロシリル基が過剰になるように設定すればよい。好ましくは得られる硬化剤の1分子中に平均で1個を超える数のヒドロシリル基が残存するように設定することが、硬化剤として使用するときの硬化性の点から好ましい。

また、本発明の硬化剤は、(b)成分を過剰の(a)成分と反応させた後に、未反応の(a)成分を蒸留、吸着、沈殿、抽出等により除去する方法によっても得ることができる。

反応温度は0～200℃、好ましくは50～150℃がよい。反応温度が0℃より低いと触媒活性が充分でなく、そのため反応速度が遅くなる。

また、150°Cより高くなると触媒が失活することが多い。

本発明の硬化剤を(a)成分と(b)成分との反応で得た場合に、硬化剤中に未反応のヒドロシリル基と場合によっては遷移金属触媒が存在するために、保存期間中にヒドロシリル基同士あるいはヒドロシリル基と系中の水が徐々に反応することにより粘度の増大やゲル化を起こす可能性がある。

これを避けるために、ヒドロシリル化反応により硬化剤を合成した後に触媒の失活を目的とした添加剤を添加してもよい。用いられる添加剤の例としては、ジメチルマレート、ベンゾチアゾール、2-ヒドロキシ-2-メチル-1-ブチン等のアセチレンアルコール類等が挙げられる。用いる添加剤の量は特に限定されないが、貯蔵安定性と硬化剤の硬化性を両立させる点から反応に用いた触媒1モルに対して1~10<sup>2</sup>モルの範囲が好ましく、より好ましくは1~30モルの範囲である。

あるいは、上記の問題を避けるために硬化剤よりヒドロシリル化触媒を除去してもよい。除去方法としては、反応溶液をシリカ、シリカゲル、アルミナ、イオン交換樹脂、活性炭等と攪拌処理、カラム処理する方法、又は中性ないし弱酸性の水溶液で水洗する方法等が例示される。

第二の硬化剤は、次の(i)、(ii)及び(iii)成分：

(i) 1分子中のケイ素原子の数が3~10個である、鎖状及び/又は環状のオルガノハイドロジエンシロキサン

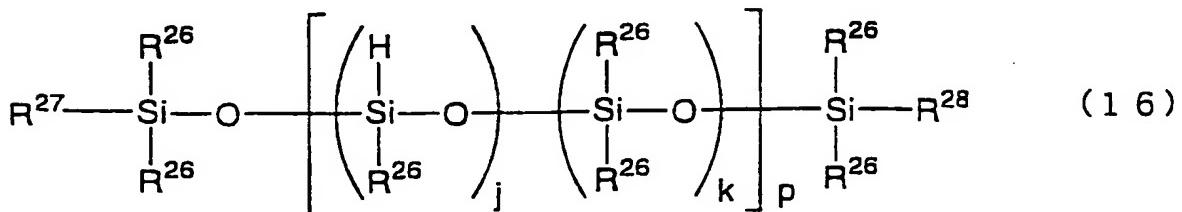
(ii) (i)成分のヒドロシリル基と反応しうる官能基を1分子中に2個以上有する化合物、

(iii) (i)成分のヒドロシリル基と反応しうる官能基を1分子中に1個含有する有機化合物

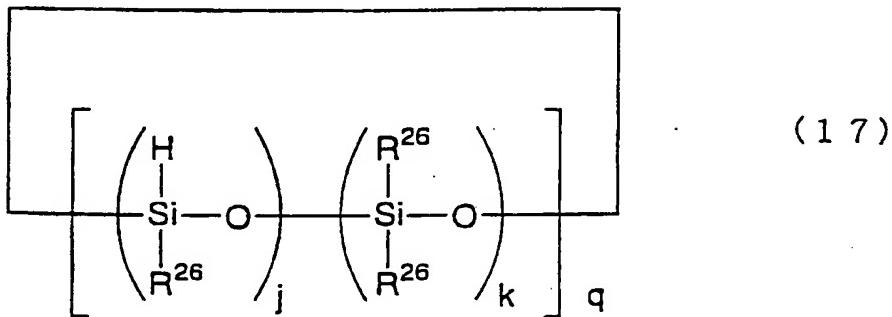
を反応することによって得られ、しかも(i)成分由来のヒドロシリル

基が実質上残存した化合物である。

上記(i)成分である鎖状又は環状のオルガノハイドロジエンシロキサンの具体的な例としては、次の一般式(16)及び(17)



(式(16)中、 $j \geq 2$ 、 $k \geq 0$ 、 $p \geq 1$ 、 $3 \leq (j+k) \times p \leq 8$ であり、 $R^{26}$ は、水素原子及び炭素数が1～20の1価の有機基より選ばれる基を表し、1個以上の芳香族置換基を含有していてもよい。それぞれの $R^{26}$ は、同じであっても異なっていてもよい。)



(式(17)中、 $j \geq 2$ 、 $k \geq 0$ 、 $q \geq 1$ 、 $3 \leq (j+k) \times q \leq 10$ であり、 $R^{26}$ は、水素原子及び炭素数が1～20の1価の有機基より選ばれる基を表し、1個以上の芳香族置換基を含有していてもよい。それぞれの $R^{26}$ は、同じであっても異なっていてもよい。)で表されるものが挙げられる。

この鎖状及び環状シロキサン1分子あたりのヒドロシリル基の数は、2個以上10個以下であることが好ましく、より好ましくは2個以上6個以下である。1分子あたりのヒドロシリル基が2個未満であると、最

終的に得られる発泡体の物理的強度が低下し、その結果収縮が抑制されにくくなり、逆に 10 個を越えると、収縮のみならず発泡体に亀裂が生じる場合がある。

上記 (i) 成分のより具体的な例としては、ポリメチルハイドロジェンシロキサン、ポリエチルハイドロジェンシロキサン、ポリフェニルハイドロジェンシロキサン等や、1, 3, 5-トリメチルシクロトリシロキサン、1, 3, 5, 7-テトラメチルシクロテトラシロキサン、1, 3, 5, 7, 9-ペンタメチルシクロペンタシロキサン、及びこれらの混合物等が挙げられる。

次に (ii) 成分である、(i) 成分のヒドロシリル基と反応しうる官能基を分子中に 2 個以上含有する化合物について述べる。

(ii) 成分の、ヒドロシリル基と反応しうる官能基としては、ビニル基、アリル基、アクリル基、メタクリル基等の炭素-炭素二重結合や、OH 基、カルボキシル基等を有する化合物が挙げられ、これらの 2 種以上が 1 分子内に存在してもよい。

炭素-炭素二重結合は分子内のどこに存在してもよいが、反応性の点から側鎖又は末端に存在するのが好ましい。1 分子中におけるヒドロシリル基と反応しうる官能基の数は、2 個以上 4 個以下が好ましく、2 個以上 3 個以下がより好ましい。1 分子中におけるヒドロシリル基と反応しうる官能基の数が 4 個を越えると、(i) 成分と (ii) 成分との反応の際にゲル状になる場合があり好ましくない。

(ii) 成分の骨格については特に制限がなく、通常の有機单量体骨格又は有機重合体骨格、水等の無機化合物が挙げられる。

有機单量体骨格としては、例えば炭化水素系、芳香族炭化水素系、フエノール系、ビスフェノール系、エポキシ樹脂モノマー、イソシアナー

ト又はこれらの混合物が挙げられる。有機重合体では、ポリエーテル系、ポリエステル系、ポリカーボネート系、飽和炭化水素系、ポリアクリル酸エステル系、ポリアミド系、ジアリルフタレート系、フェノール-ホルムアルデヒド系（フェノール樹脂系）、ポリウレタン系、ポリウレア系、メラミン系重合体、エボキシ樹脂等の骨格が挙げられる。

(ii) 成分の具体的な例としては、1, 9-デカジエン等の $\alpha$ ,  $\omega$ -アルカジエン、ジビニルベンゼン、ジアリルベンゼン、1, 4-ブタジオール及びアリルエーテル、無水フタル酸及びそのアリルエステル、O, O'-ジアリルビスフェノールA、2, 2'-ジアリルビスフェノールA、エチレングリコールあるいはジエチレングリコール及びこれらのアリルエーテル、アリル末端ポリプロピレンオキシド及びポリエチレンオキシド、無水フタル酸-エチレングリコール重合体あるいは無水フタル酸-ジエチレングリコール重合体のアリルエステル、9-デセン-1-オール、エチレングリコールモノアリルエーテル等が挙げられる。

(ii) 成分の分子量は特に限定されないが、100, 000程度以下のものが適宜使用でき、10, 000以下のものが好ましい。

次に、(iii) 成分である、(i) 成分のヒドロシリル基と反応しうる官能基を分子中に1個含有する有機化合物について述べる。

(iii) 成分の、ヒドロシリル基と反応しうる官能基としては、ビニル基、アリル基、アクリル基、メタクリル基等の炭素-炭素二重結合や、OH基、カルボキシル基等を有する化合物が挙げられる。

炭素-炭素二重結合は分子内のどこに存在してもよいが、反応性の点から側鎖又は末端に存在するのが好ましい。

(iii) 成分の骨格としては、(ii) 成分の骨格として挙げた有機單量体及び／又は有機重合体等が例示される。

(iii) 成分の具体的な例としては、1-ヘキセン、1-オクテン、1-デセン等の $\alpha$ -オレフィンや、1-プロパノール、1-オクタノール、エチレングリコールモノエチルエーテル等のアルコール類、2-エチルヘキサン酸等のカルボン酸類、アクリル酸ブチル、メタクリル酸メチル等の(メタ)アクリル類、スチレン、4-メチルスチレン、2,4-ジメチルスチレン、 $\alpha$ -メチルスチレン、4-プロモスチレン、2-ビニルナフタレン、アリルベンゼン、アリルアニソール、アリルフェニルエーテル、 $\alpha$ -アリルフェノール、 $p$ -イソプロペニルフェノール等の芳香族系化合物、片末端がアリル基、OH基、(メタ)アクリル基、カルボキシル基、他の末端がヒドロシリル基と反応しない有機基で置換されたポリオキシアルキレン、ポリエステル、アクリル重合体等が挙げられる。

(iii) 成分の分子量は特に限定されないが、100,000程度以下のものが適宜使用でき、10,000以下のものが好ましい。

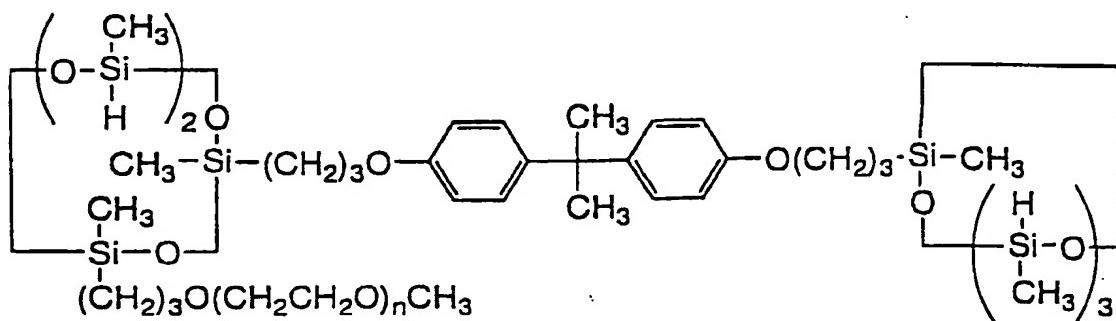
上記(i)、(ii)、(iii)各成分の混合比、すなわち(i)成分のヒドロシリル基のモル数をx、(ii)成分の(i)成分と反応しうる官能基のモル数をy、(iii)成分の(i)成分と反応しうる官能基のモル数をzとした場合の $y/x$ 及び $z/x$ の値については特に制限はないが、 $0.01 \leq y/x \leq 0.5$ 、 $0.001 \leq z/x \leq 0.8$ であることが好ましく、 $0.1 \leq y/x \leq 0.4$ 、 $0.01 \leq z/x \leq 0.4$ であることがより好ましい。

$y/x$ が0.01より小さく、相溶性が十分でなく、逆に0.5を越えると(i)成分と(ii)成分との反応時において高分子量化等に伴う粘度上昇等が起こるため好ましくない。また、 $z/x$ が0.001より小さいと系の相溶性が十分でなく、その結果発泡体のセルが荒れる等

の傾向を示すようになり、逆に 0.8 を越えると本発明の目的である収縮を抑制する効果が少なくなる傾向が生じる。

なお、(i)、(ii)、(iii) 成分をそれぞれ反応させるには、上記したヒドロシリル化触媒等を適宜用いることができる。

上記(i)成分、(ii)成分、(iii)成分を反応させて得られる化合物は、(ii)成分が多官能であるため種々の構造を有するものの混合物となるが、その一つの例としては、次式で表される化合物を含む混合物が挙げられる。なお、これらの混合物は精製せずにそのまま使用することができます。

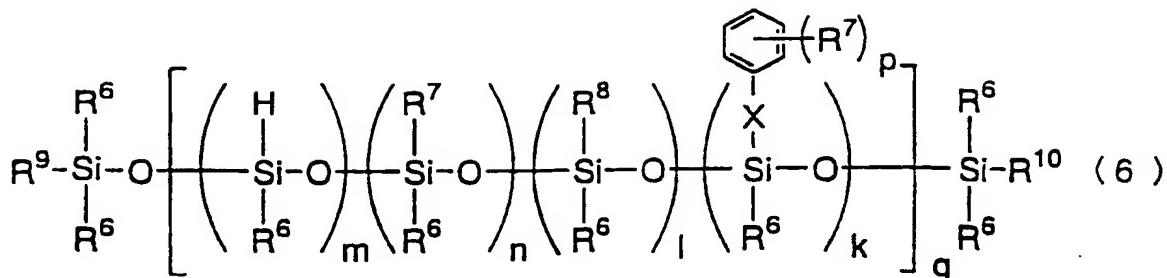


(式中、n は 1 以上 100 以下、好ましくは 40 以下の整数を示す。)

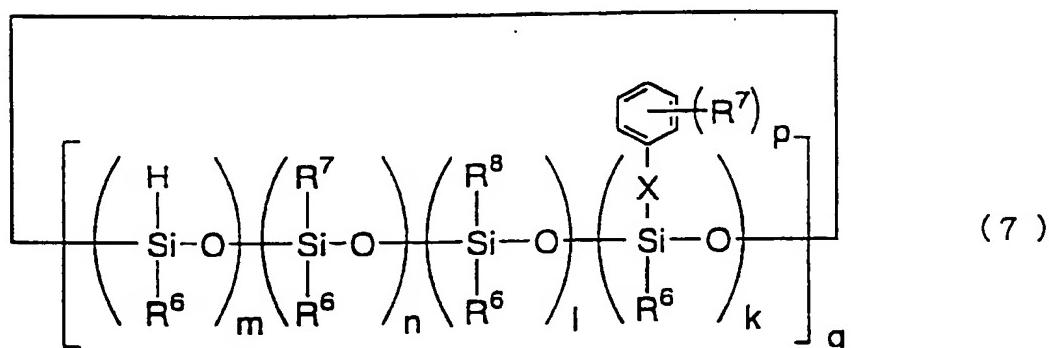
上記第一及び第二の硬化剤は、これを発泡性樹脂組成物に用いた場合に、発泡終了後の収縮が特に少ないという効果が得られる。

次に第三の硬化剤であるポリオキシアルキレン鎖及び芳香族含有有機基で変性されたポリオルガノハイドロジエンシロキサンについて述べる。

第三の硬化剤は、次の式(6)あるいは式(7)で示される構造を有する化合物である。



(式(6)中、 $m \geq 2$ 、 $n \geq 0$ 、 $l$ 、 $k$ 、 $q \geq 1$ 、 $p$ は0～5の整数、 $10 \leq (m+n+l+k) \times q \leq 80$ であり、 $\text{R}^6$ 、 $\text{R}^7$ は、炭素数0～6の1価の置換基、 $\text{R}^8$ は、分子量が100～10,000のポリオキシアルキレン鎖を示し、 $\text{R}^9$ 、 $\text{R}^{10}$ は、水素又は炭素数1～20の炭化水素基を示す。 $m$ 個、 $n$ 個、 $l$ 個、 $k$ 個の $\text{R}^6$ 、 $n$ 個、 $p$ 個の $\text{R}^7$ は、それぞれ同じものでも異なるものでもよい。Xは、構成元素としてC、H、N、O、S、ハロゲンのみを含む炭素数0～10の2価の置換基を示す。)

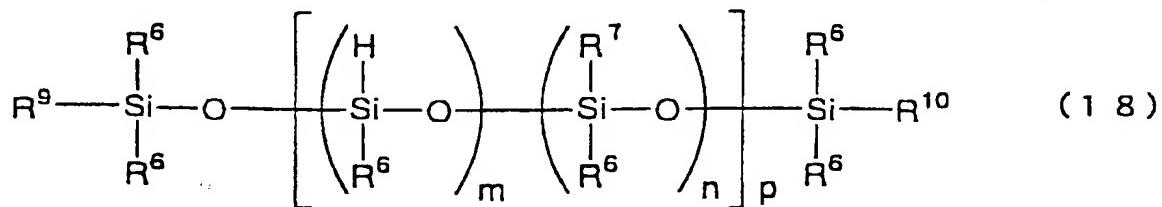


(式(7)中、 $m \geq 2$ 、 $n \geq 0$ 、 $l$ 、 $k$ 、 $q \geq 1$ 、 $p$ は0～5の整数、 $3 \leq (m+n+l+k) \times q \leq 20$ であり、 $\text{R}^6$ 、 $\text{R}^7$ 、 $\text{R}^8$ 、Xは、式(6)と同じ。)

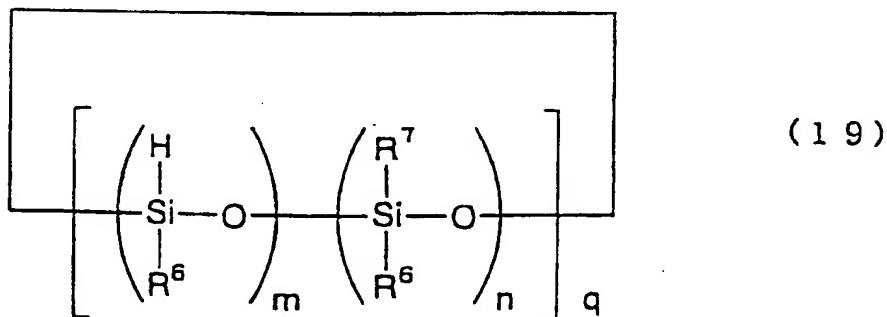
上記式(6)又は式(7)で示されるポリオルガノハイドロジエンシロキサンを得る方法としては、末端に二重結合（例えばアリル基）やOH基

等のヒドロシリル基と反応しうる官能基を有するポリオキシアルキレン化合物及び芳香環含有有機基と、ポリオルガノハイドロジェンシロキサンとの反応による方法や、予めポリオキシアルキレン鎖及び芳香環含有有機基を有する珪素化合物を用いてポリオルガノハイドロジェンシロキサンを合成する方法や、あるいは上記珪素化合物とポリオルガノシロキサンとの再分配反応等が利用できる。

具体的には、例えば次の式(18)及び式(19);



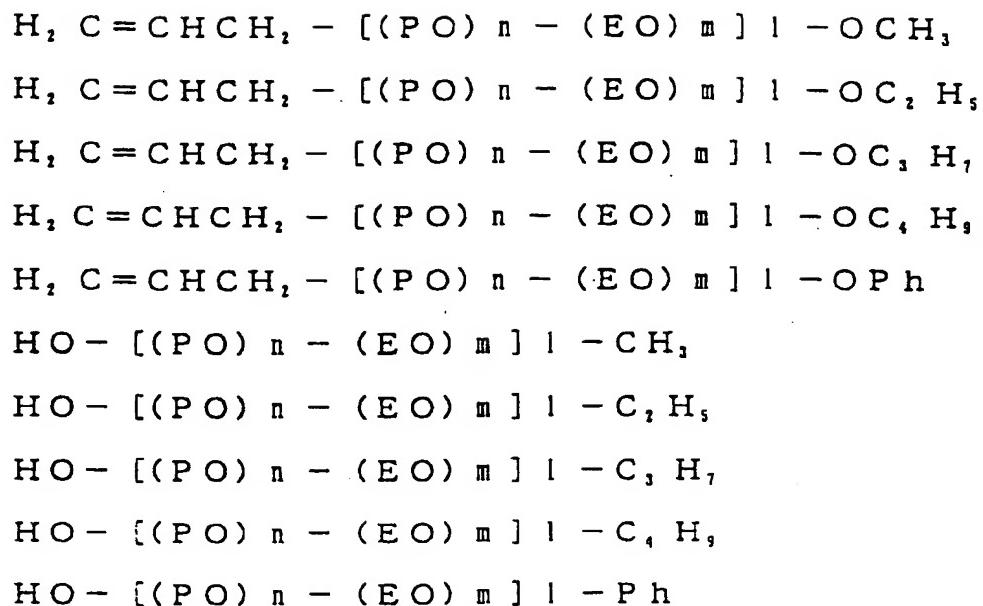
(式(18)中、 $m \geq 2$ 、 $n \geq 0$ 、 $p \geq 1$ 、 $10 \leq (m+n) \times p \leq 80$ であり、 $\text{R}^6$ 、 $\text{R}^7$ 、 $\text{R}^9$ 、 $\text{R}^{10}$ は、上記と同じ。)。



(式(19)中、 $m \geq 2$ 、 $n \geq 0$ 、 $q \geq 1$ 、 $3 \leq (m+n) \times q \leq 20$ であり、 $\text{R}^6$ 、 $\text{R}^7$ は、上記と同じ。)

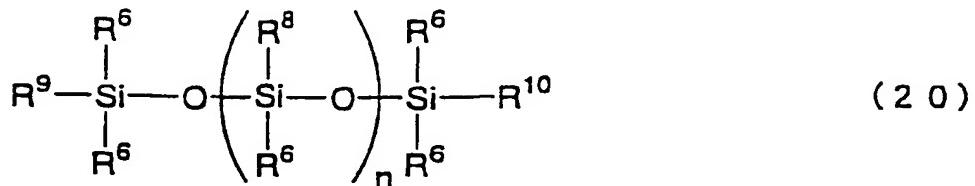
で表される鎖状、環状のポリオルガノハイドロジェンシロキサンと、



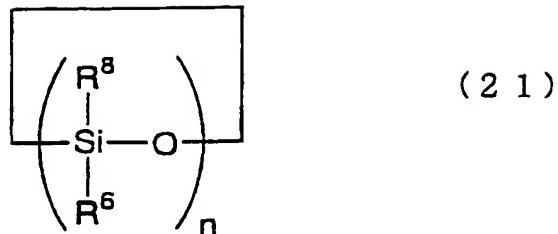


(上記各式において、 $1 \leq (m+n) \times 1 \leq 80$ 、 $m, n \geq 0$ 、 $1 \geq 1$ )  
 等のポリエーテル系化合物と、スチレン、4-メチルスチレン、2, 4-メチルスチレン、 $\alpha$ -メチルスチレン、4-プロモスチレン、2-ビニルナフタレン、アリルベンゼン、アリルアニソール、アリルフェニルエーテル、o-アリルフェノール、p-イソプロペニルフェノール、フェノール、o-クレゾール、ベンジルアルコール、フェネチルアルコール、安息香酸、4-ヒドロキシ安息香酸等の芳香環含有化合物との反応が挙げられる。

また、上記式(18)及び式(19)で表される鎖状、環状のポリオルガノハイドロジエンシロキサンと上記芳香環含有化合物との反応物と、



(式(20)中、 $5 \leq n \leq 80$ であり、 $R^6, R^8, R^9, R^{10}$ は、上記と同じ。) や、



(式(21)中、 $3 \leq n \leq 20$ であり、 $R^6$ 、 $R^8$ は、上記と同じ。)

等との再分配、平衡化反応等が挙げられる。

式(18)で表されるポリオルガノハイドロジエンシロキサンの具体的な例としては、ポリメチルハイドロジエンシロキサン、ポリエチルハイドロジエンシロキサン、ポリフェニルハイドロジエンシロキサン、メチルハイドロジエンシロキサン-ジメチルシロキサン共重合体、メチルハイドロジエンシロキサン-ジエチルシロキサン共重合体、メチルハイドロジエンシロキサン-メチルフェニルシロキサン共重合体、及びエチルハイドロジエンシロキサン-ジメチルシロキサン共重合体等が挙げられる。

また、式(19)で表されるシクロシロキサンにおけるシロキサン単位の具体的な例としては、メチルハイドロジエンシロキサン、エチルハイドロジエンシロキサン、フェニルハイドロジエンシロキサン、ジメチルシロキサン、ジエチルシロキサン、メチルフェニルシロキサン等が挙げられ、これらが共重合して環状体を成したものが用いられる。

ここで、式(6)及び式(7)に示したポリシロキサンにおいて、全シロキサン単位に対するポリオキシアルキレン基及び芳香環含有有機基が結合した珪素原子の割合、すなわち式(6)及び式(7)における

$$\left( (l+k) / (m+n+l+k) \right) \times 100 (\%)$$

を変性率を呼ぶことにする。

十分な整泡性を得るために、他成分の組成や混合比にもよるが、上記変性率は、一般的には5~90%がよく、5~25%が特に好ましい。た

だし、変性率には分布が存在するので、ここで挙げる数値は平均値とする。変性率が 5 %より低いと炭素-炭素二重結合を有する有機化合物との相溶性が悪くなり、整泡性が低下し、発泡体のセルが微細にならず、場合によっては発泡途中に破泡が生じ、十分な発泡倍率が得られないことがある。逆に変性率が 90 %より高いとヒドロシリル基当量が大きくなり、この化合物を硬化剤として単独で用いて発泡体を得るためには、多量を必要とし、発泡倍率の低い発泡体しか得られないので好ましくない。

また、上記変性率中に占める芳香環含有有機基が結合した割合、すなわち  $k / (1 + k)$  は、発泡体製造時の混合物の相溶性への悪影響を生じない範囲で任意に調節することができる。

ポリオキシアルキレン鎖の構造としては、オキシエチレン単位の割合が多いほうが好ましく、全オキシアルキレン単位に対するオキシエチレン単位の割合は、数単位で 50 ~ 100 %のものが好ましい。オキシアルキレン単位の割合がこれより小さいと十分な整泡性が得られない。

オキシアルキレン鎖の分子量は、特に限定されないが、数平均分子量で 100 ~ 3000 が好ましく、200 ~ 1000 が特に好ましい。数平均分子量が 100 より小さいと十分な整泡性が得られず、逆に 3000 より大きいとヒドロシリル基の密度が低下するため、発泡体を製造する上で十分に硬化させるには多量を用いねばならず、従って、発泡倍率の低い発泡体しか得られないので好ましくない。

上記した第一～第三の硬化剤は、1種を単独で用いてもよく、2種以上を併用してもよい。

なお、本発明の硬化剤におけるヒドロシリル基の個数については、少なくとも 1 分子中に平均して 1 個あればよいが、相溶性を損なわない限り多いほうが好ましい。本発明の硬化剤を用いてヒドロシリル化反応により炭

素-炭素二重結合を有する有機化合物を硬化させる場合、該ヒドロシリル基の個数が2個未満であると、硬化が遅く、硬化不良を起こす場合が多い。また、本発明の硬化剤を発泡性樹脂組成物に適用する場合、当該硬化剤とOH基含有化合物とが脱水素縮合して、発泡に関与するのであるから、該ヒドロシリル基の個数は、目的とする発泡倍率によって決まるが、一般に3個以上であることが好ましい。一方、当該個数の上限については、化合物の入手の容易性や発泡と硬化のバランス等から80以下が好ましく、50以下がより好ましい。

## 2. 硬化性組成物

第二の発明に係る硬化性組成物は、

- (A) 分子内に少なくとも1個のアルケニル基を含有する有機化合物、
- (B) 有機系硬化剤、
- (C) ヒドロシリル化触媒

を必須成分として含有してなるものである。各成分について以下に述べる。

### (B) 成分

本発明の(B)成分である有機系硬化剤としては、第一の発明として述べた各種の硬化剤を用いることができ、好ましい分子構造等についても第一の発明のものが適用できる。

また、(B)成分である硬化剤としては、(A)成分との相溶性に影響を与えない範囲で、ヒドロシリル基を有する他の硬化剤を併用することもできる。

### (A) 成分

本発明の(A)成分である分子中に少なくとも1個の炭素-炭素二重結合を含有する有機化合物は、骨格にシロキサン結合を実質的にもたないものであればその構造に特に制限はなく、低分子化合物、重合体等の各種分

子構造をもつものが用いられる。

(A) 成分において、その分子構造を、骨格部分と、その骨格に共有結合によって結合している炭素-炭素二重結合を有するアルケニル基とに分けて考えた場合、炭素-炭素二重結合を有するアルケニル基は分子内のどこに存在してもよいが、反応性の点から側鎖又は末端に存在するのが好ましい。

(A) 成分を具体的に例示するならば、低分子化合物としては、ジアリルフタレート等のエステル系化合物、エチレングリコールジアリルエーテル等のエーテル系化合物、2,6-ジアリルフェノール、2,2'-ジアリルビスフェノールA等のフェノール系化合物等が挙げられる。

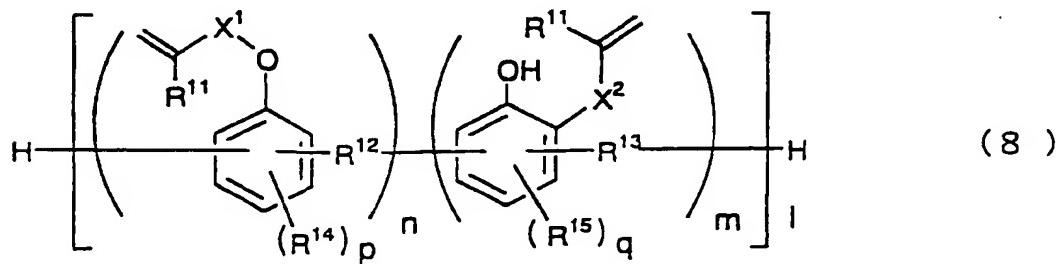
重合体としては、各種重合体の末端あるいは主鎖中にアルケニル基を導入したものが挙げられ、各種重合体の具体例としては、ポリオキシエチレン、ポリオキシプロピレン、ポリオキシテトラメチレン、ポリオキシエチレン-ポリオキシプロピレン共重合体等のポリエーテル系重合体、アジピン酸等の2塩基酸とグリコールとの縮合又はラクトン類の開環重合で得られるポリエステル系重合体、エチレン-プロピレン系共重合体、ポリイソブチレン、イソブチレンとイソブレン等との共重合体、ポリクロロブレン、ポリイソブレン、イソブレンとブタジエン、アクリロニトリル、ステレン等との共重合体、ポリブタジエン、ブタジエンとステレン、アクリロニトリル等との共重合体、ポリイソブレン、ポリブタジエン、イソブレンあるいはブタジエンとアクリロニトリル、ステレン等との共重合体を水素添加して得られるポリオレフィン系重合体、エチルアクリレート、ブチルアクリレート等のモノマーをラジカル重合して得られるポリアクリル酸エステル、エチルアクリレート、ブチルアクリレート等のアクリル酸エステルと酢酸ビニル、アクリロニトリル、メチルメタクリレート、ステレン等との

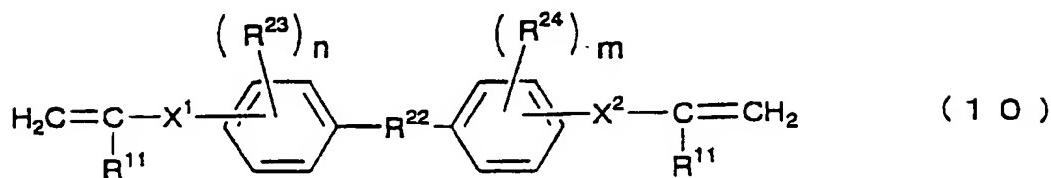
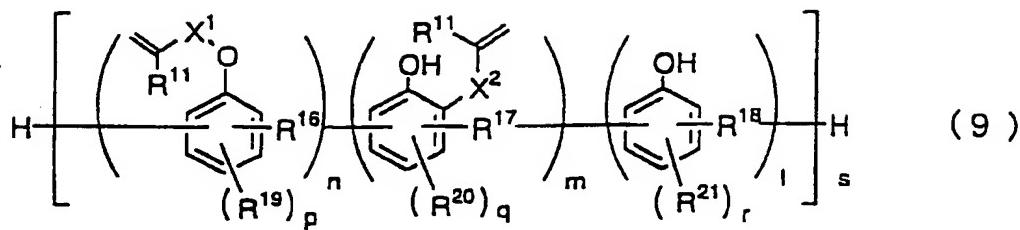
アクリル酸エステル系共重合体、前記有機重合体中でビニルモノマーを重合して得られるグラフト重合体、ポリサルファイド系重合体、 $\epsilon$ -アミノカプロラクタムの開環重合によるナイロン6、ヘキサメチレンジアミンとアジピン酸の縮重合によるナイロン66、ヘキサメチレンジアミンとセバシン酸の縮重合によるナイロン610、 $\epsilon$ -アミノウンデカン酸の縮重合によるナイロン11、 $\epsilon$ -アミノラウロラクタムの開環重合によるナイロン12、上記のナイロンのうち2成分以上の成分を有する共重合ナイロン等のポリアミド系重合体、例えばビスフェノールAと塩化カルボニルより縮重合して製造されたポリカーボネート系重合体、ジアリルフタレート系重合体、ノボラック樹脂、レゾール樹脂等のフェノール系重合体等が例示される。

上記分子構造をもつ化合物のうち、(B)成分の、ヒドロシリル基含有有機系硬化剤の極性の高い化合物との相溶性が良好であるという特長を活かすという点から、エステル系化合物、エーテル系化合物、フェノール系化合物、ポリエステル系重合体、アクリル酸エステル系重合体、アクリル酸エステル系共重合体、ポリエーテル系重合体、ポリカーボネート系重合体、フェノール系重合体が好ましい。

更に、分子内に少なくとも1個のフェノール基を含有する化合物である場合が特に好ましい。

より具体的な好ましい構造としては、下記一般式(8)～式(10)





(式(8)～式(10)において、 $\text{R}^{11}$ は、H又は $\text{CH}_3$ を示し、 $\text{R}^{12}$ 、 $\text{R}^{13}$ 、 $\text{R}^{16}$ 、 $\text{R}^{17}$ 、 $\text{R}^{18}$ 、 $\text{R}^{22}$ は、炭素数0～6の2価の置換基を示し、 $\text{R}^{14}$ 、 $\text{R}^{15}$ 、 $\text{R}^{19}$ 、 $\text{R}^{20}$ 、 $\text{R}^{21}$ 、 $\text{R}^{23}$ 、 $\text{R}^{24}$ は、炭素数0～6の1価の置換基を示し、 $\text{X}^1$ 、 $\text{X}^2$ は、炭素数0～10の2価の置換基を示す。また、式(8)において、 $n$ 、 $m$ は、0～300の整数、 $l$ は、1～300の整数、 $p$ 、 $q$ は、0～3の整数を示し、式(9)において、 $n$ 、 $m$ 、 $l$ は、0～300の整数、 $s$ は、1～300の整数、 $p$ 、 $q$ 、 $r$ は、0～3の整数を示し、式(10)において、 $n$ 、 $m$ は、0～4の整数を示す。)

のうちのいずれか1種以上の構造を分子骨格として有するものが挙げられる。

(A) 成分の分子内に少なくとも1個のアルケニル基を含有する有機化合物の製造方法としては、種々提案されているものを用いることができるが、例えば、水酸基、アルコキシド基、カルボキシル基、エポキシ基等の官能基を有する前駆体化合物に、上記官能基に対して反応性を示す活性基及びアルケニル基を有する有機化合物を反応させることによりアルケニル基を導入する方法がある。

上記官能基に対して反応性を示す活性基とアルケニル基との両方を有する有機化合物の例としては、アクリル酸、メタクリル酸、ビニル酢酸、アクリル酸クロライド、アクリル酸プロマイド等のC3～C20の不飽和脂肪酸、酸ハライド、酸無水物等やビニルアルコール、アリルアルコール、3-ブテン-1-オール、4-ベンテン-1-オール、5-ヘキセン-1-オール、6-ヘプテン-1-オール、7-オクテン-1-オール、8-ノネン-1-オール、9-デセン-1-オール、2-(アリルオキシ)エタノール、ネオペンチルグリコールモノアリルエーテル、グリセリンジアリルエーテル、トリメチロールプロパンジアリルエーテル、トリメチロールエタンジアリルエーテル、ペンタエリスリトールトリアリルエーテル、1,2,6-ヘキサントリオールジアリルエーテル、ソルビタンジアリルエーテル、ビニルベンジルアルコール等の不飽和脂肪族アルコール、アリルクロロホルメート( $\text{CH}_2=\text{CHCH}_2\text{OCOCl}$ )、アリルブロモホルメート( $\text{CH}_2=\text{CHCH}_2\text{OCOBz}$ )等のC3～C20の不飽和脂肪族アルコール置換炭酸ハライド、アリルクロライド、アリルブロマイド、ビニル(クロロメチル)ベンゼン、アリル(クロロメチル)ベンゼン、アリル(ブロモメチル)ベンゼン、アリル(クロロメトキシ)ベンゼン、1-ブテニル(クロロメチル)エーテル、1-ヘキセニル(クロロメトキシ)ベンゼン、アリルオキシ(クロロメチル)ベンゼン、アリルイソシアネート、アリルグリシジルエーテル等が挙げられる。

また、重合中にアルケニル基を導入する方法もある。例えばラジカル重合法で(A)成分の有機重合体を製造する場合に、アリルメタクリレート、アリルアクリレート等の分子中にラジカル反応性の低いアルケニル基を有するビニルモノマー、アリルメルカプタン等のラジカル反応性の低いアルケニル基を有するラジカル連鎖移動剤を用いることにより、重合体の主鎖

又は末端にアルケニル基を導入することができる。本発明の組成物を用いてゴム状硬化物を作製する場合には、(A) 成分のアルケニル基は分子末端に存在する方が硬化物の有効網目鎖長が長くなるので好ましい。

他に、エステル交換法を用いてアルケニル基を導入する方法がある。この方法はポリエステル樹脂やアクリル樹脂のエステル部分のアルコール残基をエステル交換触媒を用いてアルケニル基含有アルコール又はアルケニル基含有フェノール誘導体とエステル交換する方法である。アルコール残基との交換に用いるアルケニル基含有アルコール及びアルケニル基含有フェノール誘導体は、アリルアルコールやアリルグリコール、ビスフェノールA等の少なくとも1個のアルケニル基を有し、少なくとも1個のOH基を有するアルコール又はフェノール誘導体であればよい。触媒は使用してもしなくてもよいが、使用する場合は、酸、チタン系、アルミニウム系あるいは錫系の触媒が好ましい。具体的には、ビスフェノールA等のジアリルカーボネート、ビス(メタ)アクリル酸エステル等が挙げられる。

また、本発明の(A) 成分としては、上記のように分子内に1個以上のフェノール性水酸基を含有する化合物が好ましいが、この化合物を製造する方法としては、例えば、フェノール、クレゾール、キシレノール、レゾールシン、カテコール、ピロガロール等を用いたノボラック及び/又はレゾール型フェノールや、ビスフェノールA、ビスフェノールF、ビスフェノールS、テトラブロモビスフェノールA等のビスフェノール系化合物類に、フェノール性水酸基に対して反応性を示す活性基とアルケニル基の両方を有する有機化合物を反応させることによりアルケニル基を導入する方法が挙げられる。具体的な反応としては、O,O'-ジアリルビスフェノールA、2,2'-ジアリルビスフェノールA等のフェノール類と塩化アリル、臭化アリル等とを塩基触媒存在下で反応させる方法や、ビスフェノールA等の

フェノール類をアリルグリシジルエーテルやグリシジルメタクリレート等とエポキシ化触媒下で反応させる方法、4,4'-メチレンビス(フェニルイソシアネート)やトリレン-2,6-ジイソシアネート等のイソシアネートとアリルアルコール又はアリルアミンとをウレタン化触媒存在下で反応させる方法が例示される。また、必要に応じ、末端、主鎖あるいは側鎖にOH基、アルコキシド基、カルボキシル基、エポキシ基等の官能基を有する主鎖骨格を予め合成し、前述の方法に例示される方法によりアルケニル基を導入する方法もある。

他に、アルケニル基を有する化合物を一部又は全部に用いてフェノール樹脂骨格を合成する方法がある。これは、二重結合を有する芳香族化合物とフェノール類とを、例えば、ホルムアルデヒドやジイソシアナートにより反応させる方法であり、具体的には、アリルフェノールと他のフェノール類とを酸又は塩基存在下、ホルムアルデヒド等により、重縮合させる方法である。また、ビス(メタ)アクリル酸エステルに対し、アリルアルコール、アリルグリコール等がマイケル付加して得られるアリルエーテル系化合物等も用いることができる。

以上のようなアルケニル基と有機化合物との結合様式には特に制限はなく、炭素-炭素結合で直接結合している場合の他に、エーテル、エステル、カーボネート、アミド、ウレタン結合等を介して該アルケニル基が有機化合物に結合しているもの等が例示される。

(A) 成分の分子量については、硬化物の特性及び(B)成分との相溶性等の点から100~50000が好ましく、100~20000が特に好ましい。

(A) 成分の有機化合物の炭素-炭素二重結合の数は、1分子当たりの平均で1.0個を越えることが好ましく、特に2個以上5個以下であるこ

とが好ましい。(A) 成分の1分子内の炭素-炭素二重結合の数が1個以下の場合は、(B) 成分と反応してもグラフト構造となるのみで架橋構造とならないためである。

上記(B)成分と(A)成分の比率は、ヒドロシリル基のアルケニル基に対するモル比で0.2~5.0が好ましく、0.4~2.5がより好ましい。モル比が0.2より小さくなると、本発明の組成物を硬化した場合に硬化が不充分でペトツキのある強度の小さい硬化物しか得られず、またモル比が5.0より大きくなると硬化後も硬化物中に活性なヒドロシリル基が多量に残存するので、クラック、ポイドが発生し、均一で強度のある硬化物が得られない傾向がある。

### (C) 成分

本発明の(C)成分であるヒドロシリル化触媒については、特に制限なく任意のものが使用できる。

具体的には、第1の発明であるヒドロシリル基含有有機系硬化剤について述べたのと同様の触媒を用いることができる。これらの触媒は単独で使用してもよく、2種以上併用してもよい。触媒活性の点から塩化白金酸、白金-オレフィン錯体、白金-ビニルシロキサン錯体等が好ましい。触媒量としては特に制限はないが、(A)成分中のアルケニル基1モルに対して $10^{-1} \sim 10^{-8}$ モルの範囲で用いるのがよい。好ましくは $10^{-3} \sim 10^{-6}$ モルの範囲で用いるのがよい。

### その他の成分

硬化物を調製する際には、(A)、(B)及び(C)の三成分の他に、その使用目的に応じて溶剤、接着性改良剤、物性調整剤、保存安定性改良剤、可塑剤、充填剤、老化防止剤、紫外線吸収剤、金属不活性化剤、オゾン劣化防止剤、光安定剤、アミン系ラジカル連鎖禁止剤、リン系過酸化物分解

剤、滑剤、顔料、発泡剤、難燃剤等の各種添加剤を適宜添加できる。

上記充填剤の具体例としては、たとえば、ガラス繊維、炭素繊維、マイカ、グラファイト、ケイソウ土、白土、ヒュームシリカ、沈降性シリカ、無水ケイ酸、アルミナ、カーボンブラック、炭酸カルシウム、クレー、タルク、酸化チタン、炭酸マグネシウム、硫酸バリウム、石英、アルミニウム微粉末、フリント粉末、亜鉛末、無機バルーン、ゴムグラニュー、木粉、フェノール樹脂、メラミン樹脂、塩化ビニル樹脂等が挙げられる。

上記老化防止剤としては、一般に用いられている老化防止剤、たとえばクエン酸やリン酸、硫黄系老化防止剤等が用いられる。

上記硫黄系老化防止剤としては、メルカプタン類、メルカブタンの塩類、スルフィドカルボン酸エステル類や、ヒンダードフェノール系スルフィド類を含むスルフィド類、ポリスルフィド類、ジチオカルボン酸塩類、チオウレア類、チオホスフェイト類、スルホニウム化合物、チオアルデヒド類、チオケトン類、メルカプタール類、メルカプトール類、モノチオ酸類、ポリチオ酸類、チオアミド類、スルホキシド類等が挙げられる。

上記ラジカル禁止剤としては、たとえば 2, 2'-メチレンービス(4-メチル-6-t-ブチルフェノール)、テトラキス(メチレン-3(3, 5-ジ-t-ブチル-4-ヒドロキシフェニル)プロピオネート)メタン等のフェノール系ラジカル禁止剤や、フェニル-β-ナフチルアミン、α-ナフチルアミン、N, N'-第二ブチル-p-フェニレンジアミン、フェノチアジン、N, N'-ジフェニル-p-フェニレンジアミン等のアミン系ラジカル禁止剤等が挙げられる。

上記紫外線吸収剤としては、例えば 2(2'-ヒドロキシ-3', 5'-ジ-t-ブチルフェニル)ベンゾトリアゾール、ビス(2, 2, 6, 6-テトラメチル-4-ビペリジン)セバケート等が挙げられる。

上記接着性改良剤としては、一般に用いられている接着剤やアミノシラ

ン化合物、エポキシシラン化合物等のシランカップリング剤、その他の化合物を用いることができる。このような接着性改良剤の具体例としては、フェノール樹脂、エポキシ樹脂、 $\gamma$ -アミノプロピルトリメトキシシラン、N-( $\beta$ -アミノエチル)アミノプロピルメチルジメトキシシラン、クマロン-インデン樹脂、ロジンエステル樹脂、テルペン-フェノール樹脂、 $\alpha$ -メチルスチレン-ビニルトルエン共重合体、ポリエチルメチルスチレン、アルキルチタネート類、芳香族ポリイソシアネート等を挙げることができる。

上記難燃剤としては、テトラブロモビスフェノールA、テトラブロモビスフェノールAエポキシ、デカブロモジフェニルオキサイド等のハロゲン系剤、トリエチルホスフェート、トリクロレジルホスフェート、トリス(クロロエチル)ホスフェート、トリス(クロロプロピル)ホスフェート、トリス(ジクロロプロピル)ホスフェート、ポリ磷酸アンモニウム、赤磷等の燐系難燃剤、水酸化アルミニウム、水酸化マグネシウム、三酸化アンチモン、五酸化アンチモン等の無機系難燃剤等があげられる。これら難燃剤は、1種を単独で使用しても、2種以上を併用してもよい。

#### 硬化物の製造

上記(A)及び(B)成分、好ましくはさらに(C)成分、必要に応じてさらにその他の添加成分を混合し、硬化させれば発泡等の現象を伴うことなく、深部硬化性に優れた均一な硬化物が得られる。

硬化物の性状は、用いる(A)及び(B)成分の重合体の主鎖骨格や分子量等に依存するが、ゴム状のものから樹脂状のものまで製造することが可能である。

硬化条件については特に制限はないが、一般に0~200°Cで10秒~4時間、好ましくは30~150°Cで10秒~4時間硬化するのがよい。

特に 80 ~ 150°C の高温では 10 秒 ~ 1 時間程度の短時間で硬化するものも得られる。

組成物の配合方法については特に限定はないが、作業性の面から硬化性組成物の (A)、(B) 成分それぞれを実質的な成分とする 2 種以上の組成物を調製した後、それらを混合することにより、硬化させることが望ましい。触媒である (C) 成分の添加方法にも特に制限はなく、作業上容易な方法を選択すればよく、(A) 成分と (B) 成分のどちらかに混合して用いても、また、(A) 成分、(B) 成分の混合と同時に、又は、混合終了後に添加しても良い。

硬化物製造の具体的な方法としては、本発明の硬化性組成物と触媒、さらに必要に応じて添加剤を適当な組み合わせで事前に混合した 2 液又はそれ以上の数の別々の混合物を使用直前に混合し、押出、又は注入させる方法が望ましい。混合方法としては、特に限定されないが、ハンドミキシング、電動ミキサー、スタティックミキサー、衝突混合等の通常、ウレタン樹脂、エポキシ樹脂、フェノール樹脂で使用されている方法を用いることができる。

### 3. 発泡性樹脂組成物

第三の発明に係る発泡性樹脂組成物は、第二の発明の硬化性組成物に、(D) 発泡剤及び／又は OH 基を有する化合物をさらに必須成分として含有してなるものである。

本発明の発泡性樹脂組成物においては、(A) 成分と (B) 成分とが耐候性に優れた Si-C 結合を生成するヒドロシリル化反応によって付加型の架橋反応を行うことにより硬化し、これと同時に前記 (A) 成分と (B) 成分との反応熱により発泡剤が気化又は分解し、あるいは (B) 成分と (D) 成分とが反応して水素ガスを発生することにより発泡し、発泡体が形成さ

れる。

すなわち、本発明の発泡性樹脂組成物では、(A) 成分として分子骨格中にシロキサン単位を含まない有機化合物を用いることにより、前記先行技術に開示されたごときシリコーンフォームに比べ、圧縮強度、塗装性、接着性、汚染性、埃付着性等が向上したものが得られる。

また、(B) 成分を種々に変化させることにより、硬質から半硬質及び軟質といった幅広い物性を有するものが得られる。

特に、(B) 成分として特定の構造を有する化合物を用いることにより、発泡倍率が高く、かつ独立気泡率の高い発泡体を得ることができる。

本発明の(B) 成分である有機系硬化剤としては、第一の発明で説明した各種の硬化剤を用いることができ、好ましい分子構造、他の硬化剤との併用等についても第一及び第二の発明で述べたものが適用できる。

本発明の(A) 成分である分子中に少なくとも1個の炭素-炭素二重結合を含有する有機化合物としては特に制限はなく、第二の発明で説明したとおりの低分子化合物、重合体等の各種分子構造をもつものを使用することができます。

(A) 成分の骨格は、(B) 成分との相溶性が良好であるという特長を活かすものであることが好ましく、ポリシロキサン-有機ブロックコポリマーやポリシロキサン-有機グラフトコポリマーのようなシロキサン単位(Si-O-Si)は含まず、構成元素として炭素、酸素、水素、窒素、イオウ、ハロゲンのうちのいずれか1種以上のみを含む骨格であるものが好ましい。例えば、ポリエーテル系、ポリエステル系、ポリカーボネート系、飽和炭化水素系、ポリアクリル酸エステル系、ポリアミド系、フェノール-ホルムアルデヒド系(フェノール樹脂系)等の骨格である。また单量体骨格としては、例えばフェノール系、ビスフェノール系、又はこれらの混

合物が挙げられる。

これらのうち、ポリエーテル系重合体骨格は、軟質の発泡体を得るために好適に使用される。その例としては、ポリオキシエチレン、ポリオキシプロピレン、ポリオキシテトラメチレン、ポリオキシエチレン-ポリオキシプロピレン共重合体等が挙げられる。

一方、ポリシロキサン骨格に比べて  $T_g$  が高い、その他の重合体骨格も発泡体を得るために好適に使用される。

また、(A) 成分の有機化合物は、他の成分との均一な混合が可能で、スプレー、注入等により発泡体が得られるように、100°C以下の温度において流動性があることが好ましい。その構造は線状でも枝分かれ状でもよく、分子量は特に限定されないが、100～100,000程度の任意のものが好適に使用でき、有機重合体であれば、500～20,000のものが特に好ましい。分子量が500未満では可とう性の付与等の有機重合体の利用による特徴が発現し難く、分子量が100,000を越えるとアルケニル基とヒドロシリル基との反応による架橋の効果が発現し難い傾向がある。

#### (D) 成分

次に (D) 成分の発泡剤及びOH基を有する化合物について述べる。発泡剤とOH基を有する化合物については、それぞれ単独で用いても併用しても良い。

発泡剤の種類に特に制限はなく、例えば、通常、ポリウレタン、フェノール、ポリスチレン、ポリオレフィン等の有機発泡体に用いられるものから選択して用いることが可能である。安定した発泡体を製造するには、揮発性化合物を発泡剤として予め組成物に添加し、発熱や減圧により発泡させる方法が好ましい。

発泡剤が揮発性化合物の場合には、その沸点は100°C以下が好ましく、

80℃以下がより好ましく、50℃以下が特に好ましい。使用する装置や取り扱いの容易さ等を考えると、沸点が-30℃から35℃程度のものが好ましい。

また、発泡剤の(A)成分に対する溶解度は、23℃において(A)成分100重量部に対し5重量部以上が好ましく、10重量部以上がより好ましく、15重量部以上がさらに好ましい。溶解度が5重量部より少ないと、発泡体のセルが荒れるので好ましくなく、また、所望の高倍率の発泡体が得られにくい。

発泡剤の(A)成分に対する溶解度は、例えば次の方法により求められる。すなわち発泡剤の沸点が23℃以上であれば、(A)成分の重量と、発泡剤を溶解させた後の重量を測定し、その差を求めればよく、また、発泡剤の沸点が23℃未満である等の理由で上記方法により測定が困難な場合には、体積既知の耐圧容器に(A)成分と発泡剤を秤量したのち、耐圧容器の空隙部の体積と圧力から、溶解していない発泡剤の量を求め、これに基づいて溶解度を求めることができる。

発泡剤の種類は特に限定されないが、作業性と安全性との面から、炭化水素、ケトン系化合物、フロン、エーテル等の有機化合物、二酸化炭素、窒素、空気等から選ばれる化合物を単独あるいは2種以上併用して用いることが好ましい。

炭化水素としては、メタン、エタン、プロパン、n-ブタン、イソブタン、n-ペンタン、イソペンタン、ネオペンタン、n-ヘキサン、2-メチルベンタン、3-メチルベンタン、2,2-ジメチルブタン、2,3-ジメチルブタン、シクロベンタン、シクロブタン、シクロベンタン、シクロヘキサン等が挙げられる。これらのうち、取り扱いの容易さ等からプロパン、n-ブタン、イソブタン、n-ペンタン、シクロベンタンが好ましい。

ケトン系化合物の例としては、アセトン、メチルエチルケトン、メチルイソプロピルケトン等が挙げられる。

フロン類としては、トリクロロフルオロメタン（R 1 1）、ジクロロジフルオロメタン（R 1 2）、クロロトリフルオロメタン（R 1 3）、プロモトリフルオロメタン（R 1 3 B 1）、テトラフルオロメタン（R 1 4）、ジクロロフルオロメタン（R 2 1）、クロロジフルオロメタン（R 2 2）、トリフルオロメタン（R 2 3）、ジフルオロメタン（R 3 2）、フルオロメタン（R 4 1）、テトラクロロジフルオロエタン（R 1 1 2）、トリクロロトリフルオロエタン（R 1 1 3）、ジクロロテトラフルオロエタン（R 1 1 4）、ジブロモテトラフルオロエタン（R 1 1 4 B 2）、クロロベンタフルオロエタン（R 1 1 5）、ヘキサフルオロエタン（R 1 1 6）、クロロトリフルオロエタン（R 1 2 3）、テトラフルオロエタン（R 1 3 4 a）、ジクロロフルオロエタン（R 1 4 1 b）、クロロジフルオロエタン（R 1 4 2 b）、ジフルオロエタン（R 1 5 2 a）、オクタフルオロプロパン（R 2 1 8）、ジクロロベンタフルオロプロパン（R 2 2 5）、ヘキサフルオロプロパン（R 2 3 6 e a）、ベンタフルオロプロパン（R 2 4 5 f a）、オクタフルオロシクロブタン（R C 3 1 8）、ヘキサフルオロブタン（R 3 5 6 m f f m）、ペンタフルオロブタン（R 3 6 5 m f c）、デカフルオロベンタン（R 4 3 1 0 m e e）等が挙げられる。

環境問題等を考慮すると、クロロフルオロカーボン（CFC）よりは、ハイドロクロロフルオロカーボン（HCFC）、いわゆる代替フロンが好ましく、更にハイドロフルオロカーボン（HFC）を使用するのが特に好ましい。すなわち、テトラフルオロエタン、ジフルオロエタン、オクタフルオロプロパン、ヘキサフルオロプロパン、ベンタフルオロプロパン、オクタフルオロシクロブタン、ヘキサフルオロブタン、ペンタフルオロブタン

が特に優れている。

エーテル類としては、ジメチルエーテル、ジエチルエーテル、エチルメチルエーテル、ジプロピルエーテル、ジイソプロピルエーテル、ブチルメチルエーテル、ブチルエチルエーテル、*t e r t*-ブチルメチルエーテル、*t e r t*-ブチルエチルエーテル、1,1-ジメチルプロピルメチルエーテル、メチルペンタフルオロエチルエーテル、2,2,2-トリフルオロエチルエーテル、メチル(トリフルオロメチル)テトラフルオロエチルエーテル等が挙げられる。

上記の中でも好適に用いられる発泡剤としては、(A) 成分の構造等にもよるが、炭化水素類やフロン類等が挙げられ、これらの中でも(A)成分100重量部に対する23℃における溶解度が5重量部以上である炭素数2又は3のハイドロフルオロカーボン(HFC)、炭素数1から3のハイドロクロロフルオロカーボン(HCFC)、炭素数3~6の炭化水素、炭素数3~5のケトン系化合物、及び炭素数2~6のエーテル類のうちから選ばれるいずれか1種以上が特に好適に用いられる。環境問題等の点からは、炭化水素、ハイドロクロロフルオロカーボン(HCFC)、ハイドロフルオロカーボン(HFC)が好ましい。

また、他の発泡方法として、例えばNaHCO<sub>3</sub>、(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>、NH<sub>4</sub>HCO<sub>3</sub>、NH<sub>4</sub>NO<sub>2</sub>、Ca(N<sub>3</sub>)<sub>2</sub>、NaBH<sub>4</sub>等の無機系発泡剤、アゾジカルボンアミド、アゾビスイソブチロニトリル、バリウムアゾジカルボキシレート、ジニトロソベンタメチレンテトラミン、パラトルエンスルホニルヒドラジッド等の有機系発泡剤、イソシアネートと活性水素基含有化合物との反応による二酸化炭素の発生、機械的な攪拌等等を併用することも可能である。

次に、OH基を有する化合物について述べる。

本発明で用いるOH基を有する化合物の種類は特に限定されないが、従来のシリコーンフォームで多く用いられているOH基含有（ポリ）シロキサンではなく、他の成分との相溶性が良好であり、シロキサン結合を分子骨格中に含まないものが好ましい。具体的には、OH基が炭素原子と直接結合している有機化合物及び水のいずれか一方又は両方を用いるのが好ましく、これにより炭素-炭素二重結合を有する有機化合物を使用する効果がより顕著になる。OH基が炭素原子と直接結合している化合物とは、アルコール類、カルボン酸類等である。

アルコール類としては、メタノール、エタノール、n-プロパノール、iso-プロパノール、n-ブタノール、iso-ブタノール、tert-ブタノール、エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールモノプロピルエーテル、エチレングリコールモノブチルエーテル、ジエチレングリコールモノメチルエーテル、エチレングリコールモノフェニルエーテル、エチレングリコールモノアリルエーテル、グリセリンジアリルエーテル等の1価のアルコール、エチレングリコール、プロピレングリコール、1,4-ブチレングリコール、1,3-ブチレングリコール、2,3-ブチレングリコール、ジエチレングリコール、トリエチレングリコール、ネオペンチルグリコール、1,6-ヘキサメチレングリコール、1,9-ノナメチレングリコール、グリセリン、トリメチロールプロパン、ペンタエリスリトール、ソルビトール、スクロース、グリセリンモノアリルエーテル等の多価アルコール、ポリプロピレングリコール、ポリエチレングリコール及びこれらの共重合体、ポリテトラメチレングリコール等のポリエーテルポリオール（ソルビトール、スクロース、テトラエチレンジアミン、エチレンジアミン等を開始剤とした一分子内にOH基を3個以上含むものも含む）、アジペート系ポリオール、

ポリカプロラクトン系ポリオール、ポリカーボネート系ポリオール等のポリエステルポリオール、エポキシ変性ポリオール、ポリエーテルエステルポリオール、ベンジリックエーテル型フェノールポリオール等のフェノール系ポリオール、ルミフロン（旭硝子社製）等のフッ素ポリオール、ポリブタジエンポリオール、水添ポリブタジエンポリオール、ひまし油系ポリオール、ハロゲン含有難燃性ポリオール、リン含有難燃性ポリオール、フェノール、クレゾール、キシレノール、レゾルシン、カテコール、ピロガロール、ビスフェノールA、ビスフェノールB、ビスフェノールS、フェノール樹脂等のフェノール性水酸基を有する化合物、2-ヒドロキシエチル（メタ）アクリレート、2-ヒドロキシプロピル（メタ）アクリレート、2-ヒドロキシエチルビニルエーテル、N-メチロール（メタ）アクリルアミド、東亜合成化学工業（株）製のアロニクス5700、4-ヒドロキシスチレン、日本触媒化学工業（株）製のHE-10、HE-20、HP-10及びHP-20（いずれも末端にOH基を有するアクリル酸エステルオリゴマー）、日本油脂（株）製のブレンマーPPシリーズ（ポリプロピレングリコールメタクリレート）、ブレンマーPEシリーズ（ポリエチレングリコールモノメタクリレート）、ブレンマーPEPシリーズ（ポリエチレングリコールポリプロピレングリコールメタクリレート）、ブレンマーAP-400（ポリプロピレングリコールモノアクリレート）、ブレンマーAE-350（ポリエチレングリコールモノアクリレート）、ブレンマーNKH-5050（ポリプロピレングリコールポリトリメチレンモノアクリレート）及びブレンマーGLM（グリセロールモノメタクリレート）、OH基含有ビニル系化合物とε-カプロラクトンとの反応により得られるε-カブロラクトン変性ヒドロキシアルキルビニル系モノマー等のOH基含有ビニル系モノマー（これらは（A）成分と（D）成分の兼用物質としても利用

できる)、前記OH基含有ビニル系モノマーとアクリル酸、メタクリル酸、それらの誘導体等との共重合により得ることができるOH基を有するアクリル樹脂、その他アルキド樹脂、エポキシ樹脂等のOH基を有する樹脂が挙げられる。

これらのOH基含有化合物の中でも、硬化反応時の発熱による蒸発・気化等によって気泡の合一、肥大化、破泡等の悪影響を及ぼさないことから、炭素数3以上のアルコールが望ましく、具体的には、n-プロパノール、iso-プロパノール、n-ブタノール、iso-ブタノール、tert-ブタノール、エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールモノプロピルエーテル、エチレングリコールモノブチルエーテル、ジエチレングリコールモノメチルエーテル等が好ましい。さらにヒドロシリル基との反応の容易さや脱水素縮合が進行しても架橋が起こらないこと、及び取扱いの際の臭気の面から、n-プロパノール、n-ブタノール、エチレングリコールモノメチルエーテル、ジエチレングリコールモノメチルエーテル、エチレングリコールモノフェニルエーテル等の1級アルコールが特に好ましい。

一方、カルボン酸類としては、酢酸、プロピオン酸、n-酪酸、イソ酪酸、n-吉草酸、ヘキサン酸、2-エチルヘキサン酸、マロン酸、こはく酸、アジピン酸、meso-1,2,3,4-テトラカルボン酸、安息香酸、フタル酸、イソフタル酸、テレフタル酸等が挙げられる。この中でも、ヒドロシリル基との反応の容易さや脱水素縮合が進行しても架橋が起こらないことから1価のカルボン酸が好ましく、さらに取扱時の臭気の面から2-エチルヘキサン酸が特に好ましい。

水酸基当量が大きくなると添加するOH基含有化合物の体積が大きくなり、発泡倍率が上がらなくなるため、水酸基当量が1~33mmol/g

の化合物が好ましく、反応性の点から $2.5 \sim 25 \text{ mmol/g}$ のものがより好ましい。

また発泡速度の調整のために2種類以上のOH化合物を併用することも可能である。併用する例としては、n-ブロパノール等の1級アルコールとiso-ブロパノール等の2級アルコール、カルボン酸と1級アルコール、あるいはカルボン酸と水との組み合わせが好ましい。さらに硬化時間の調整のためにエチレングリコール、プロピレングリコール、1,4-ブタンジオール、グリセリン等の2価以上の多価OH化合物やエチレングリコールモノアリルエーテル、グリセリンモノアリルエーテル、グリセリンジアリルエーテル、ペンタエリスリトールジアリルエーテル、ペンタエリスリトールトリアリルエーテル、ウンデシレン酸等の分子内にヒドロシリル化可能な炭素-炭素二重結合とOH基との両方を合わせ持つ化合物を使用することもできる。

なお、1分子内に2個以上のOH基を有する(D)成分を用いた場合は、(B)成分と(D)成分との反応で水素ガスを発生するとともに架橋構造を作るため、硬化時間の調整のために少量を補助的に使用することは可能であるが、多量に用いるのは十分な発泡を行う前に硬化してしまうために望ましくない。また、1分子内に炭素-炭素二重結合とOH基とを有する化合物を(A)成分と(D)成分の兼用物質として用いることもできる。

上記(A)、(B)、(D)の3成分の配合割合は、各成分の構造、目的とする発泡倍率、目的とする物性により適宜選択されるものであって特に限定はされないが、(B)成分のヒドロシリル基のモル数xと、(A)成分の炭素-炭素二重結合のモル数y及び(D)成分のOH基のモル数zの和との比率が、 $x : y + z = 30 : 1 \sim 1 : 30$ であることが好ましい。さらに好ましくは、 $x : y + z = 10 : 1 \sim 1 : 10$ である。ヒドロシリル基

のモル比が  $x : y + z = 30 : 1$  を越えると架橋密度が低くなり、十分な機械的強度が得られず、 $x : y + z = 1 : 30$  未満であると十分な発泡、硬化が起こらない。

また、(A) 成分の炭素-炭素二重結合のモル数  $y$  と (D) 成分のOH基のモル数  $z$  との比率には特に限定はなく、目的とする発泡倍率、目的とする物性、(B) 成分の骨格、(D) 成分の種類等により、適宜選定することができるが、一般的には  $y : z = 100 : 1 \sim 1 : 100$  が好ましく、 $y : z = 10 : 1 \sim 1 : 20$  がより好ましい。

なお、本発明では、前記(B)成分と(D)成分との脱水素縮合、及び(A)成分と(B)成分との付加反応(ヒドロシリル化反応)のための触媒を適宜用いることができる。

ヒドロシリル化触媒及び助触媒の種類、使用量等は、第一及び第二の発明に関し述べたものが本発明にも適用できる。

#### その他の成分

本発明の発泡性樹脂組成物には、さらに充填剤、老化防止剤、ラジカル禁止剤、紫外線吸収剤、接着性改良剤、難燃剤、ポリジメチルシロキサン-ポリアルキレンオキシド系界面活性剤あるいは有機界面活性剤(ポリエチレングリコールアルキルフェニルエーテル等)等の整泡剤、酸あるいは塩基性化合物(ヒドロシリル基とOH基との反応調整のための添加剤であり、酸で縮合反応を抑制し、塩基で加速する。)、保存安定改良剤、オゾン劣化防止剤、光安定剤、増粘剤、可塑剤、カップリング剤、酸化防止剤、熱安定剤、導電性付与剤、帶電防止剤、放射線遮断剤、核剤、リン系過酸化物分解剤、滑剤、顔料、金属不活性化剤、物性調整剤等を本発明の目的及び効果を損なわない範囲において添加することができる。

上記充填剤、老化防止剤、ラジカル禁止剤、紫外線吸収剤、接着性改良

剤、難燃剤の例は、第二の発明で説明したとおりである。

### 発泡体の製造

上記した本発明の発泡性樹脂組成物に、必要に応じて触媒その他の添加剤を混合し、発泡硬化させることにより発泡体が製造される。

発泡硬化させる温度は、100°C以下が好ましく、現場発泡への適用を考えると常温に近いのがより好ましい。100°Cを越える高温では、(A)成分と(B)成分との付加型の架橋(硬化)反応速度が大きくなりすぎ、(B)成分と(D)成分との反応で発生する水素ガスによる発泡とのバランスがとり難い。

また、本発明に係る発泡体の製造は、本発明の発泡性樹脂組成物と触媒、さらに必要に応じて添加剤を適当に組み合わせて事前に混合した2液又はそれ以上の数の別々の混合物を使用直前に混合し、基材表面に直接塗布し、現場発泡させる方法や、同様の混合物を使用直前に混合し、注入発泡させる方法により行うことができる。混合方法としてはハンドミキシング、電動ミキサー、スタティックミキサー、衝突混合等の方法を用いることができる。特に現場発泡させる場合にはスタティックミキサー又は衝突混合を用いることが好ましい。

本発明の発泡性樹脂組成物と触媒とを、さらに必要に応じて添加剤を事前に混合した2液又はそれ以上の数の別々の混合物とする場合の組み合わせ方としては次のようなものが挙げられるが、すべての成分を混合する前に水素の発生や硬化が進行しない組み合わせであればよく、これらには限は定されない。すなわち、

(1) (B)成分の一部及び(A)成分の混合物と、(B)成分の一部、(D)成分及び(C)成分との混合物との2液とする、

(2) (A)成分、(D)成分及び(C)成分の混合物と、(B)成分のみと

の 2 液とする、あるいは、

(3) (A) 成分、(D) 成分及び(C) 成分の混合物と、(B) 成分及び(D) 成分の混合物との 2 液とする、等である。

発泡体の成形方法も特に制限されず、押出し発泡法、連続発泡方法、注型成形方法、不連続成形方法、又は現場発泡施工方法等、ポリウレタンフォーム、フェノールフォーム、シリコーンフォーム等の製造に使用される各種発泡成形方法が適宜利用できる。

上記連続発泡方法としては、ベルトコンベア上に連続的に繰り出される紙又はプラスチックフィルムの上で自由に発泡させるスラブ発泡法や、紙、ペニヤ板、金属板等の面材とともに成形し、ラミネートするダブルコンベア法等が用いられる。注型成形方法は、所望形状の型内に吐出発泡させ、キュア硬化させて型の内面形状に添った成形品を作り上げる方法である。不連続成形方法は、サンドイッチパネル等の成形に用いられる。

現場施工方法としては、一液型簡易スプレー法、二液型スプレー法、二液型注入法、二液型塗布法等があり、主に建築断熱用途に用いられる。

本発明における発泡体は、(発泡体の体積) / (発泡体の体積 - 発泡体中の空隙の体積) として表した、単位体積当たりの発泡倍率において特に制限はないが、発泡体であることによる有用な特徴が顕著となる 2 倍以上、特に 4 倍以上の発泡倍率を有するのが好ましい。

上記したように、本発明の発泡性樹脂組成物は、常温あるいは比較的低温の加熱下において発泡するので現場発泡が可能であり、またイソシアネートを含まず低毒性で、かつ発泡倍率を上げることにより単位体積当たりの価格を下げることが可能であるという効果を有する。

また、この発泡性樹脂組成物を用いることを特徴とする本発明の製造方法によれば、耐候性、塗装性、接着性が良好であり、燃焼時に有害なガス

の発生がないという優れた特徴を有する発泡体が得られる。

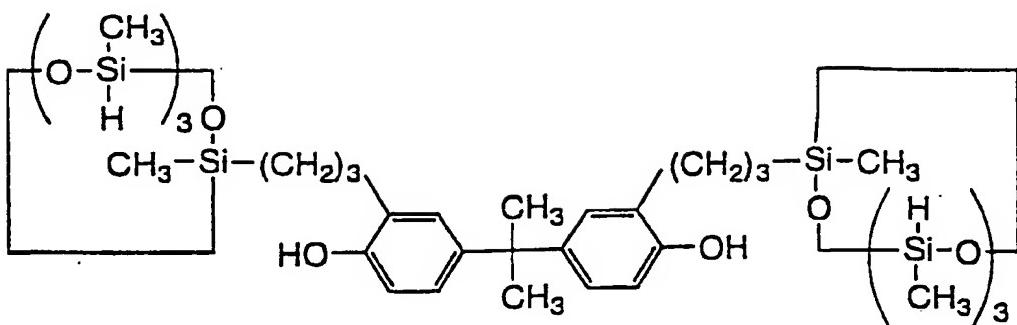
しかも、(A) 成分の組成（骨格と架橋点間分子量）や各成分の配合比率等の選択により、硬質発泡体から軟質発泡体まで製造可能で、発泡倍率も低倍率から高倍率まで設定できる。さらに、化学発泡と架橋の反応速度をコントロールが可能であることや、(B) 成分に特定の構造を持つ化合物を用いることにより、セル構造が微細で均一な発泡体を製造することが可能となる。

#### [実施例]

次に、本発明を実施例によってさらに具体的に説明する。ただし、本発明は以下の実施例に限定されるものではない。

#### 合成例 1

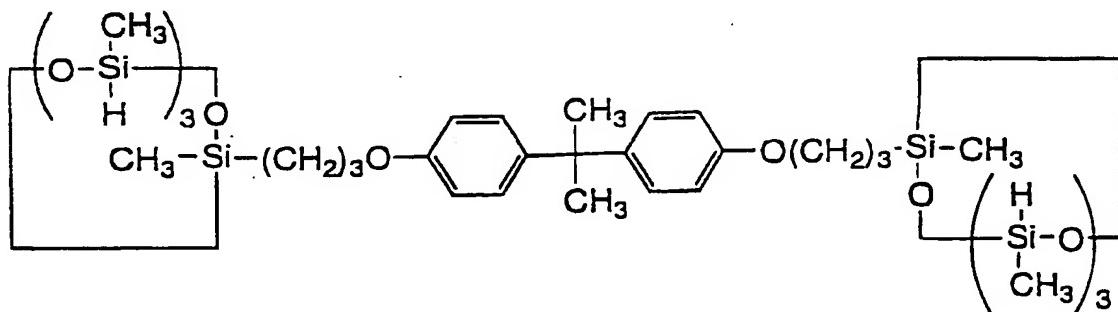
温度計、攪拌装置子、滴下漏斗、コンテンサーを備えた3Lの四首丸底フラスコに、窒素雰囲気下、1, 3, 5, 7-テトラメチルシクロテトラシロキサン（信越化学（株）製 KF9902）1504g及びトルエン500m<sup>l</sup>を入れた。室温にて攪拌下、白金-ビニルシロキサン錯体のキシレン溶液47.2μl（白金原子にして $6.2 \times 10^{-6}$ m<sup>o</sup>l）をトルエン20m<sup>l</sup>に溶解させ添加した。70℃に加温して攪拌下、2, 2'-ジアリルビスフェノールA 192gをトルエン200m<sup>l</sup>に溶解させたものを30分かけて滴下漏斗から添加した。添加終了後、滴下漏斗をトルエン30m<sup>l</sup>で洗浄した。得られた溶液を70℃で2時間攪拌した後、ベンゾチアゾール16.7mgを添加した。減圧下にトルエン及び未反応のテトラメチルシクロテトラシロキサンを留去して、470gの茶色の粘稠な液体を得た。このものの核磁気共鳴、質量分析、赤外分光分析等の分析により、式；



で表される化合物と同定された。

### 合成例 2

温度計、攪拌装置子、滴下漏斗、コンデンサーを備えた2Lの四首丸底フラスコに、窒素雰囲気下、1, 3, 5, 7-テトラメチルシクロテトラシロキサン500g及びトルエン150mlを入れた。室温にて攪拌下、白金-ビニルシロキサン錯体のキシレン溶液15.6μlをトルエン20mlに溶解させ添加した。70℃に加温して攪拌下、ビスフェノールAジアリルエーテル64.1gをトルエン60mlに溶解させたものを30分かけて滴下漏斗から添加した。添加終了後、滴下漏斗をトルエン20mlで洗浄した。得られた溶液を70℃で2時間攪拌した後、ベンゾチアゾール4.7mgを添加した。減圧下にトルエン及び未反応のテトラメチルシクロテトラシロキサンを留去して、165gの薄黄色のやや粘稠な液体を得た。このものの核磁気共鳴、質量分析、赤外分光分析等の分析により、式：



で表される化合物と同定された。

### 合成例 3

1リットルの四つ口フラスコに、攪拌棒、滴下ロート、上部に3方コックを付けた冷却管、温度計をセットした。このフラスコに1、3、5、7-テトラメチルシクロテトラシロキサン120g、白金-ビニルシロキサン錯体のキシレン溶液241μl)、トルエン120mlを入れた。混合液を80℃に加熱し、滴下ロートからO-アリルフェノール67.0g(0.50mol)を20分かけて滴下した。80℃でそのまま2時間攪拌した。

反応混合物を核磁気共鳴の測定により、ビニル基のピークが消失したことを確認し、冷却した後、活性炭10gを加え、室温で1時間攪拌した。混合物を濾過し、濾液を濃縮することにより、3-(2-ヒドロキシフェニル)プロピル基で変性したメチルハイドロジェンシクロシロキサンをやや粘稠液体として得た。このポリシロキサンのS<sub>i</sub>H値を測定したところ、8.1mmol/gであった。

### 合成例 4

滴下ロート、上部に3方コックを接続した冷却管、温度計、メカニカルスターーラーを接続した4つ口フラスコ内に、1、3、5、7-テトラメチルシクロテトラシロキサン60.1gを入れ、3方コックより酸素／窒素混合ガス（酸素含有量1%）を流しながら40℃に加熱した。Pt-ビニルシロキサン（3%キシレン溶液）6.5mgを入れ、滴下ロートよりO,O'-ジアリルビスフェノールA30.8gを滴下し、その後末端がアリル基およびメチル基で置換されたポリエチレンオキシド重合体（数平均分子量400）8.1gを滴下した。そのまま40度で1時間攪拌し、反応を完結させたのち、安定剤としてベンゾチアゾールを添加した。反応混合物を減圧下で加熱し揮発分を留去することによりやや粘調な透明液体を得た。

合成例 5

1リットルの四つ口フラスコに、攪拌棒、滴下ロート、上部に三方コックを付けた冷却管、温度計をセットした。このフラスコに1, 3, 5, 7-テトラメチルシクロテトラシロキサン120g、白金-ビニルシロキサン錯体のキシレン溶液241μlを入れた。混合液を40℃に加熱し、滴下ロートから $\alpha$ -メチルスチレン11.8g(0.10mol)を5分かけて滴下した。30分攪拌後、反応混合物を<sup>1</sup>H-NMRによりビニル基のピークが消失したことを確認し、次に片末端がメチル基、もう一方の末端がアリル基でそれぞれ変性されたエチレンオキシド重合体(数平均分子量350)70g(アリル基0.20mol)を10分かけて滴下し、終了後80℃でそのまま2時間攪拌した。

反応混合物を<sup>1</sup>H-NMRにより、ビニル基のピークが消失したことを確認し、冷却した後、活性炭10gを加え、室温で1時間攪拌した。混合物を濾過し、フェネチル基およびポリオキシアルキレン基で変性したシクロテトラシロキサンを粘稠液体として得た。このポリシロキサンのS i H値を測定したところ、8.3mmol/gであった。

合成例 6

合成例4に準じて、1, 3, 5, 7-テトラメチルシクロテトラシロキサンの代わりに、ポリオルガノハイドロジェンシロキサン(信越化学(株)製 KF-99)120g、トルエン120ml、白金-ビニルシロキサン錯体のキシレン溶液241μlを入れた。混合液を80℃に加熱し、合成例5と同様に、滴下ロートから $\alpha$ -メチルスチレン11.8g、エチレンオキシド重合体70gを10分かけて滴下し、終了後80℃でそのまま2時間攪拌した。

反応混合物を<sup>1</sup>H-NMRにより、ビニル基のピークが消失したことを

確認し、冷却した後、活性炭 10 g を加え、室温で 1 時間攪拌した。混合物を濾過し、濾液を濃縮することにより、フェネチル基およびポリオキシアルキレン基で変性したメチルハイドロジェンポリシロキサンを粘稠液体として得た。このポリシロキサンの SiH 値を測定したところ、8.3 mmol/g であった。

#### 合成例 7

合成例 6 に準じて、 $\alpha$ -メチルスチレンを用いずにポリオキシエチレン重合体 70 g のみを用いて反応させたほかは同様の操作を行い、ポリオキシエチレン基で変性したメチルハイドロジェンポリシロキサンを粘稠液体として得た。このポリシロキサンの SiH 値を測定したところ、9.3 mmol/g であった。

#### 合成例 8

合成例 6 に準じて、ポリオキシエチレン重合体を用いずに、 $\alpha$ -メチルスチレン 47.2 g のみを用いて反応させたほかは同様の操作を行い、変性したメチルハイドロジェンシロキサンを粘調液体として得た。SiH 値は 9.6 mmol/g であった。

#### 合成例 9

温度計、還流冷却器、滴下ロート、攪拌モータを備えた四つロフラスコに、ノボラック型フェノール樹脂 (PSM4261、群栄化学(株) 製、OH 含量 9.71 mmol/g) 36.9 g 及びアセトン 160 ml を入れ、攪拌しながら炭酸カリウム 50 g を添加した。アリルプロマイド 5.2 g を少量づつ滴下したのち、55 ℃で 6 時間反応させた。これをろ過し、濃縮して、アルカリ、酸の順で洗浄し、珪酸アルミニウム 7.4 g を添加して攪拌した後、さらにろ過、濃縮して、ヨウ素価により測定した不飽和基含量が 7.3 mmol/g の生成物 40 g を得た。この生成物は、核磁

気共鳴の測定により水酸基がアリル化されたO-アリル化ノボラック型フェノール樹脂であることが確認された。

#### 合成例 1

合成例 3 で得られたO-アリル化ノボラック型フェノール樹脂 40 g を空素雰囲気下で攪拌しながら 180 °C で 3 時間加熱して、ヨウ素価により測定した不飽和基含量が 7.3 mmol/g の転位生成物 40 g を得た。この生成物は、核磁気共鳴の測定によりアリル基が C laisen 転位した C-アリル化ノボラック型フェノール樹脂であることが確認された。

#### 実施例 1

合成例 1 で合成した化合物 7.9 g 及び、2,2'-ジアリルビスフェノール A 9.2 g を混合し、白金-ビニルシロキサン錯体のキシレン溶液 0.47 μl (白金原子にして  $6.0 \times 10^{-8}$  mol) を加えてさらに混合した。この混合物はほぼ透明であり、両者の相溶性が良好なことが示された。この混合物は、厚さ 3 mm になるように型枠に流し込み、50 °C で 3 時間静置して脱泡した後、150 °C で 1 時間加熱することにより硬化して均一透明な成形体を与えた。

#### 実施例 2

2,2'-ジアリルビスフェノール A 9.2 g のかわりに、2,2'-ジアリルビスフェノール A 7.4 g およびビスフェノール A ジアリルエーテル 1.8 g の混合物を用いた以外は実施例 1 と同様の操作を行った。その結果混合物は完全に透明であり、硬化して均一透明な成形体を与えた。

#### 比較例 1

合成例 1 で合成した化合物 7.9 g のかわりに合成例 2 で合成した化合物 7.9 g を用いた以外は実施例 1 と同様の操作を行った。その結果混合物は白濁し相溶しなかった。また、加熱しても得られたものは不均一であ

り良好な硬化物を与えたかった。

#### 比較例 2

合成例 1 で合成した化合物 7. 9 g のかわりに合成例 2 で合成した化合物 7. 9 g を用いた以外は実施例 2 と同様の操作を行った。その結果混合物は白濁し相溶しなかった。また、加熱しても得られたものは不均一であり良好な硬化物を与えたかった。

#### 実施例 3

合成例 1 で合成した化合物 7. 9 g、及び合成例 9 で合成した化合物 9. 2 g を用い、実施例 1 と同様の操作を行った。混合物の相溶性は良好であり、加熱により均一透明な硬化物が得られた。

#### 実施例 4

実施例 3 に準じて、合成例 9 で合成した化合物の代わりに、合成例 10 で合成した化合物 9. 2 g を利用したほかは実施例 3 と同様の操作を行った。混合物の相溶性は良好であり、加熱により均一透明な硬化物が得られた。

#### 実施例 5

実施例 1 に準じて、合成例 1 で合成した化合物のかわりに、合成例 3 で合成した化合物 7. 7 g を用いて同様の操作を行った。混合物の相溶性は良好であり、加熱により均一透明な硬化物が得られた。

#### 実施例 6

実施例 1 に準じて、合成例 1 で合成した化合物のかわりに、合成例 4 で合成した化合物 7. 9 g を用いて同様の操作を行った。混合物の相溶性は良好であり、加熱により均一透明な硬化物が得られた。

#### 実施例 7

実施例 1 に準じて、合成例 1 で合成した化合物のかわりに、合成例 5 で

合成した化合物 7. 2 g を用いて同様の操作を行った。混合物の相溶性は良好であり、加熱により均一透明な硬化物が得られた。

#### 実施例 8

実施例 1 に準じて、合成例 1 で合成した化合物のかわりに、合成例 6 で合成した化合物 7. 2 g を用いて同様の操作を行った。混合物の相溶性は良好であり、加熱により均一透明な硬化物が得られた。

#### 比較例 3

実施例 1 に準じて、合成例 1 で合成した化合物のかわりに、合成例 7 で合成した化合物 6. 6 g を用いて同様の操作を行った。その結果混合物は白濁し相溶しなかった。また、加熱しても得られたものは不均一であり良好な硬化物を与えなかった。

#### 比較例 4

実施例 1 に準じて、合成例 1 で合成した化合物のかわりに、合成例 7 で合成した化合物 6. 3 g を用いて同様の操作を行った。その結果混合物は白濁し相溶しなかった。また、加熱しても得られたものは不均一であり良好な硬化物を与えなかった。

#### 比較例 5

実施例 1 に準じて、合成例 1 で合成した化合物のかわりに、ポリメチルハイドロジエンシロキサン (KF-99) 3. 9 g を用いて同様の操作を行った。その結果混合物は白濁し相溶しなかった。また、加熱しても得られたものは不均一であり良好な硬化物を与えなかった。

#### 比較例 6

実施例 1 に準じて、合成例 1 で合成した化合物のかわりに、1, 3, 5, 7-テトラメチルシクロテトラシロキサン (KF-9902) 3. 9 g を用いて同様の操作を行った。その結果混合物は白濁し相溶しなかった。ま

た、加熱しても得られたものは不均一であり良好な硬化物を与えたかった。

#### 実施例 9

実施例 1 に準じて、合成例 1 で合成した化合物 7. 9 g、末端アリルエーテル化ポリプロピレンオキシド（数平均分子量約 8000）240 g を用いて同様の操作を行った。混合物の相溶性は良好であり、加熱により均一透明な硬化物が得られた。

#### 実施例 10

実施例 1 に準じて、合成例 1 で合成した化合物 7. 9 g、末端アリルエステル化フタル酸／ジエチレングリコール共重合体（数平均分子量約 1000）30 g を用いて同様の操作を行った。混合物の相溶性は良好であり、加熱により均一透明な硬化物が得られた。

#### 実施例 11

2, 2' -ジアリルビスフェノール A 10. 8 g（ビニル基 0. 070 mol）、合成例 1 で製造したヒドロシリル基を含有する化合物 9. 20 g（SiH 基 0. 070 mol）、および n-ブタン 1. 5 g を混合し均一液とした。ここに、白金-ビニルシロキサンのキシレン溶液（白金原子で 3. 0 重量%）43 mg を加えて 10 秒間激しく攪拌混合したところ発熱しながら発泡し、硬質の発泡体が得られた。発泡体を 23°C で 24 時間静置し、発泡終了直後に対する寸法変化を百分率で表す（以下収縮率と称する）と 5% 以下であった。得られた発泡体から立方体を切り出し、重量を測定し密度を求めたところ、27. 5 kg/m<sup>3</sup> であった。ASTM-D 2856 に準じて独立気泡率を測定したところ、85% であった。

#### 実施例 12

2, 2' -ジアリルビスフェノール A 10. 8 g のかわりに、2, 2' -ジアリルビスフェノール A 5. 39 g（ビニル基 0. 035 mol）と

ビスフェノールAジアリルエーテル5.39g（ビニル基0.035mol）の混合物を用いた以外は実施例11と同様の操作を行った。得られた発泡体の収縮率は5%以下、密度は22.8kg/m<sup>3</sup>、独立気泡率は82%であった。

#### 実施例13

合成例1で製造したヒドロシリル基を含有する化合物9.20gのかわりに、合成例3で製造したヒドロシリル基を含有する化合物8.64gを用いた以外は実施例11と同様の操作を行った。得られた発泡体の密度は27.8kg/m<sup>3</sup>、独立気泡率は70%であった。

#### 実施例14

2,2'-ジアリルビスフェノールA10.8gのかわりに、合成例9で製造したO-アリル化ノボラック型フェノール樹脂4.8g（ビニル基0.035mol）と合成例10で製造したC-アリル化ノボラック型フェノール樹脂4.8g（ビニル基0.035mol）の混合物を用いた以外は実施例11と同様の操作を行った。得られた発泡体の収縮率は5%以下、密度は38.5kg/m<sup>3</sup>、独立気泡率は60%であった。

#### 実施例15

n-ブタン1.5gのかわりに2-エチルヘキサン酸3.6g（0.025mol）を用いた以外は実施例11と同様の操作を行った。発泡体の密度は45.9kg/m<sup>3</sup>、独立気泡率は61%であった。

#### 実施例16

合成例1で製造したヒドロシリル基を含有する化合物9.20gのかわりに、合成例1で製造したヒドロシリル基を含有する化合物4.60g（SiH基0.035mol）と合成例6で製造した変性メチルハイドロジエンポリシロキサン5.21g（SiH基0.035mol）との混合物を

用いた以外は実施例 1 1 と同様の操作を行った。得られた発泡体の密度は 24.3 g / m<sup>3</sup>、独立気泡率は 72 % であった。

#### 実施例 1 7

2,2'-ジアリルビスフェノール A 10.8 g (ビニル基 0.070 mol)、合成例 4 で製造したヒドロシリル基を含有する化合物 9.20 g (SiH 基 0.070 mol)、および HFC 245fa 3.0 g を混合し均一液とした。実施例 1 1 と同様に白金-ビニルシロキサン溶液を加えて 10 秒間激しく攪拌混合したところ発熱しながら発泡し、硬質の発泡体が得られた。得られた発泡体の収縮率は 5 ~ 10 %、密度は 30.5 kg / m<sup>3</sup>、独立気泡率は 85 % であった。

#### 実施例 1 8

合成例 4 で製造したヒドロシリル基を含有する化合物のかわりに、合成例 5 で製造した変性シロキサン 8.43 g を用いた以外は実施例 1 1 と同様の操作を行った。得られた発泡体の収縮率は 30 % であったが、密度は 50 kg / m<sup>3</sup>、独立気泡率は 60 % であった。

#### 実施例 1 9

合成例 4 で製造したヒドロシリル基を含有する化合物のかわりに、合成例 6 で製造した変性シロキサン 9.2 g を用いた以外は実施例 1 1 と同様の操作を行った。得られた発泡体の収縮率は 30 % であったが、密度は 50 kg / m<sup>3</sup>、独立気泡率は 60 % であった。

#### 実施例 1 9

実施例 9 で用いたポリプロピレンオキシド 280 g、合成例 4 で製造したヒドロシリル基を含有する化合物 9.20 g、および HFC 245fa 10.0 g を混合し均一液とした。実施例 1 1 と同様に白金-ビニルシロキサン溶液を加えて 10 秒間激しく攪拌混合したところ発熱しながら発泡

し、軟質の発泡体が得られた。得られた発泡体の密度は  $200 \text{ kg/m}^3$  であった。

#### 実施例 2 0

実施例 1 0 で用いた末端アリルエステル化フタル酸／ジエチレングリコール共重合体 3.5 g、合成例 4 で製造したヒドロシリル基を含有する化合物 9.20 g、および HFC 245fa 8.0 g を混合し均一液とした。実施例 1 1 と同様に白金－ビニルシロキサン溶液を加えて 10 秒間激しく攪拌混合したところ発熱しながら発泡し、軟質の発泡体が得られた。得られた発泡体の密度は  $70 \text{ kg/m}^3$  であった。

#### 比較例 7

合成例 1 で製造したヒドロシリル基を含有する化合物のかわりに、1, 3, 5, 7-テトラメチルシクロテトラシロキサン 4.20 g を用いた以外は実施例 1 1 と同様の操作を行った。その結果アリル化合物と SiH 化合物は相溶せず、発泡体を形成しなかった。

#### 比較例 8

合成例 1 で製造したヒドロシリル基を含有する化合物のかわりに、合成例 7 で製造した変性ポリメチルハイドロジエンシロキサン 7.29 g を用いた以外は実施例 1 1 と同様の操作を行った。得られた発泡体は  $80 \text{ kg/m}^3$ 、独立気泡率は 30 % であった。

#### 比較例 9

合成例 1 で製造したヒドロシリル基を含有する化合物のかわりに、合成例 8 で製造した変性ポリメチルハイドロジエンシロキサン 7.53 g を用いた以外は実施例 1 1 と同様の操作を行った。得られた発泡体の密度を求めたところ、 $33 \text{ kg/m}^3$  であった。独立気泡率を測定したところ、10 % であった。

## 産業上の利用可能性

本発明によれば、極性の高い炭素－炭素二重結合含有有機系化合物とも十分な相溶性を有する硬化剤及び該硬化剤を用いた硬化性組成物及び発泡性樹脂組成物を提供することができる。

本発明の硬化剤を用いた硬化性組成物は、機械的強度に優れ、透明性等の外観にも優れるため、その用途は特に限定されず、一般の広い用途に使用することができる。

その例としては、例えば、電機・電子部品等の封止材料、自動車用アンダーボディーコート・建築用防水コーティング等のコーティング剤、ガスケット材料、シーリング材、ゴム・樹脂等の各種成形材料、液状・粉体状等の各種塗料、接着剤、あるいは物性改良剤・相溶化剤等の樹脂改質剤等が挙げられる。

また、本発明の発泡性樹脂組成物によれば、常温あるいは比較的低温の加熱下において発泡硬化させることができ、かつ発泡倍率が高く、しかも独立気泡率が高い発泡体が得られる。従って、高い発泡倍率により単位体積当たりの価格を下げることができるとともに、高い独立気泡率により断熱性能が良い発泡体を得ることができるので、防音、断熱、止水、気密、制振、保護、クッション、装飾等の種々の用途に広く適用することができる。

その具体例としては、特に限定されるわけではないが、例えば、車両用のクッション材、天井材、ドアトリム中材、フロアクッション制振吸音材、カーカーラー断熱材、ダンパー用エアーシール材、防水材、ガスケット、エアフィルター、センターピラーガーニッシュ、ヘッドライナー、クオータートリム、ダストカバー、燃料タンク内セーフティーフォーム、オイル

フィルター、フレキシブルコンテナー、クラッシュパッド、サンバイザー、ヘッドレスト、インシュレーター、ダッシュボード、ドアパネル、ピラー、コンソールボックス、エネルギー吸収バンパー、冷凍車・保冷車・タンクローリー車・冷凍コンテナー車等の断熱材、ガード防音材等、船舶用の断熱材、浮力材、F R P ボード芯材、ブイ等、寝装品用のクッション材等、家具等のクッション材、パッキング材等、電気・電子機器用のフィルター、吸音断熱材、プリンター吸音材、ヘッドホーンイヤーパット等、包装用の緩衝材、建築用では屋根・天井・壁・床の断熱材、水道配管等のカバー、ドアパネル、サイジングパネル、金属・サイジングパネル等の芯材、間仕切りパネルの芯材、畳・ふすま芯材、バスタブ等の断熱保温芯材、目地材、シーリング材、接着剤、システム天井断熱パネル、屋上断熱防水材、冷凍倉庫・気密倉庫等の気密断熱材、プラントのタンク・配管の保温・保冷材等、家電用では冷蔵庫・冷凍庫・電子ジャー等の断熱材、ルームクーラーの結露防止材、また、スポーツ用品や医療品及び化粧用パフ、肩パット、スリッパ、サンダル、剣山、玩具等の生活用品用途が挙げられる。

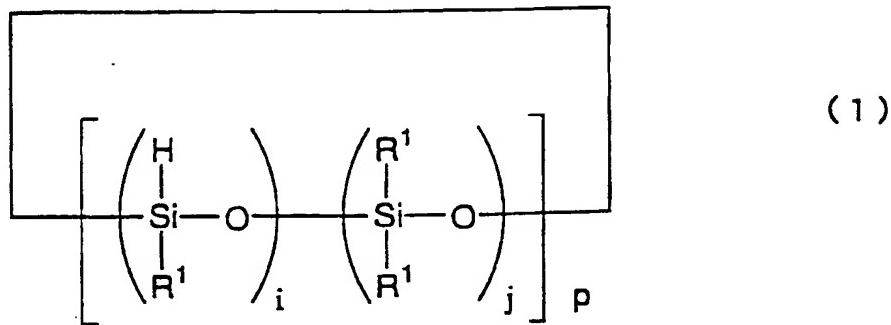
また、本発明の発泡性樹脂組成物、これを用いた発泡体及びその製造方法は、注型法における物品形状の型取りや、型からのモデルサンプル作製や装飾品作製などにも利用できるものである。

## 請求の範囲

1. 分子中に少なくとも1個の炭素-炭素二重結合を含有する有機化合物を硬化させる硬化剤であって、

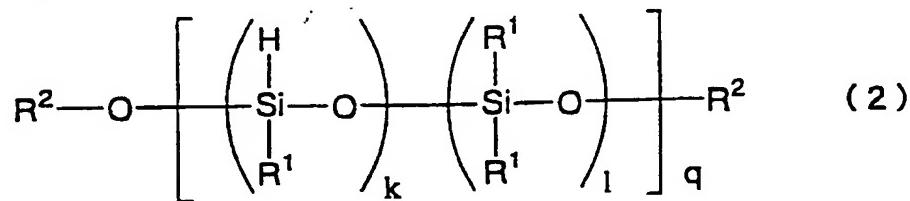
前記炭素-炭素二重結合を含有する有機化合物との相溶性が良好であることを特徴とする有機系硬化剤。

2. (a) 下記一般式(1)



(式(1)中、R'は、水素原子及び炭素数が1～20の一価の有機基より選ばれる基を表し、それぞれのR'は同じであっても異なっていてもよい。  
 $i \geq 2$ 、jは0又は正の数、 $p \geq 1$ であり、かつi、j及びpは、 $3 \leq (i + j) \times p \leq 50$ を満足する数である。)

で表される環状オリゴシロキサン及び/又は下記一般式(2)



(式(2)中、R<sup>1</sup>は上記に同じ、R<sup>2</sup>は、水素原子、-Si(CH<sub>3</sub>)<sub>3</sub>、-Si(CH<sub>3</sub>)<sub>2</sub>H及び炭素数が1～20の一価の有機基より選ばれる基を表し、それぞれのR<sup>3</sup>は同じであっても異なっていてもよい。k≥2、lは0又は正の数、q≥1であり、かつk、l及びqは、2≤(k+1)×q≤50を満足する数である。)

で表される鎖状ポリシロキサンと、

(b) 下記一般式(3)



(式(3)中、m及びnはそれぞれ独立に1～3の数を表し、pは0～2の数を表す。R<sup>3</sup>は、1個以上の炭素-炭素二重結合を含有する炭素数1～25の一価の有機基を表し、mが2以上の場合、それぞれのR<sup>3</sup>は同じであっても異なっていてもよい。R<sup>4</sup>は、ハロゲン原子、炭素数1～6のアルコキシ基、炭素数1～25の一価の有機基より選ばれる一価の基を表し、pが2の場合、それぞれのR<sup>4</sup>は同じであっても異なっていてもよい。)

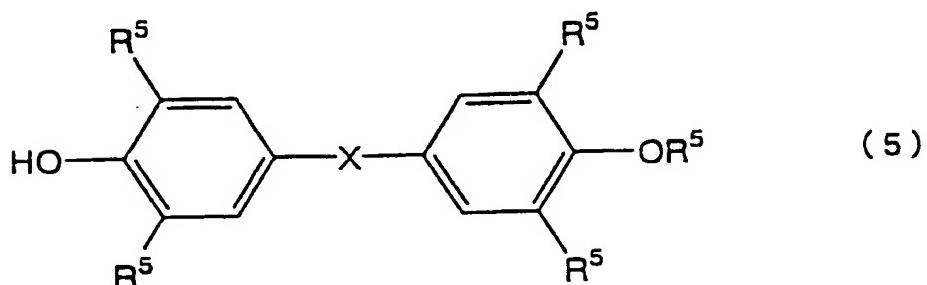
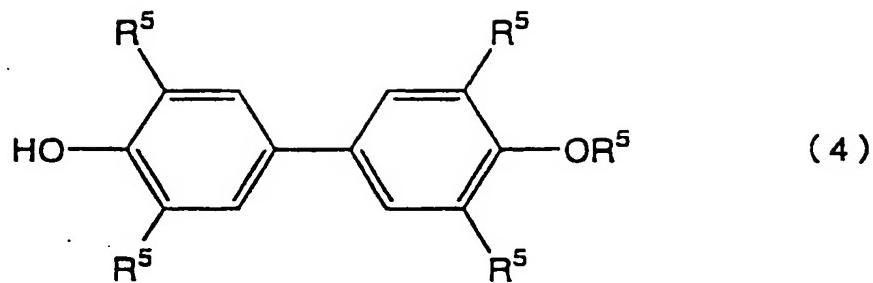
で表される分子内に1個以上の炭素-炭素二重結合及び1個以上のフェノール性水酸基を有する化合物

とを反応させて得られる請求の範囲第1項記載の硬化剤。

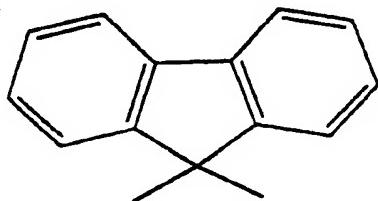
3. 前記j及びn又はlが0である請求の範囲第2項記載の硬化剤。

4. 前記iが、3≤i≤7を満足する数であり、及びn又は前記kが、2≤k≤10を満足する数である請求の範囲第3項記載の硬化剤。

5. 前記(b)成分として、下記一般式(4)又は(5)



(式(4)及び式(5)中、R<sup>5</sup>は、水素原子あるいは1個以上の炭素-炭素二重結合を含有する炭素数1～10の一価の有機基を表し、それぞれのR<sup>5</sup>は同じであっても異なっていてもよい。式(5)中、Xは、-CH<sub>2</sub>-、-C(CH<sub>3</sub>)<sub>2</sub>-、-CH(CH<sub>3</sub>)-、-C(CF<sub>3</sub>)<sub>2</sub>-、-CO-、-SO<sub>2</sub>-、-O-、あるいは式：



で表される基より選ばれる二価の置換基を示す。)

で表される分子内に1個以上の炭素-炭素二重結合及び1個以上のフェノール性水酸基を有する化合物を含有することを特徴とする、請求の範囲第2～4項のいずれか1項に記載の硬化剤。

6. (i) 1分子中のケイ素原子の数が3～10個である、鎖状及び／又は環状のオルガノハイドロジエンシロキサン、

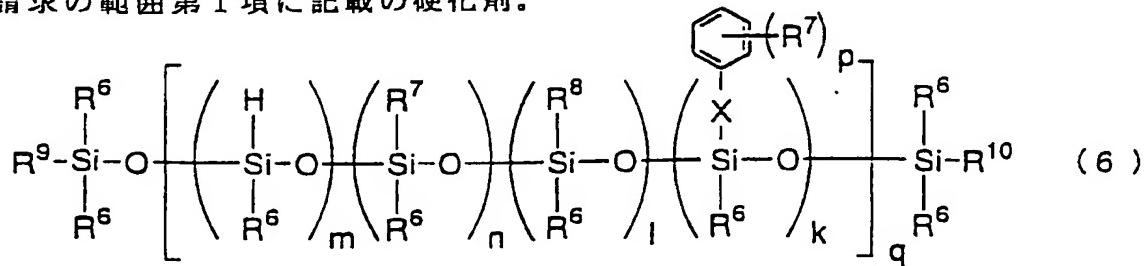
(ii) 前記(i)成分のヒドロシリル基と反応しうる官能基を1分子中

に 2 個以上有する化合物、及び

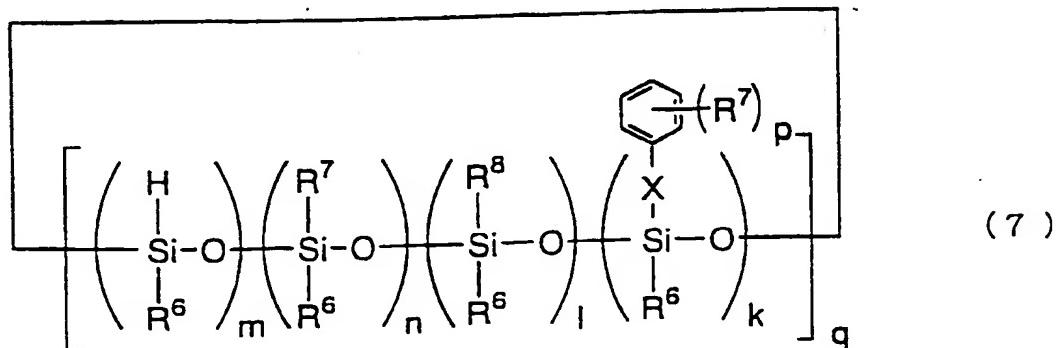
(iii) 前記 (i) 成分のヒドロシリル基と反応しうる官能基を 1 分子中に 1 個含有する有機化合物

を反応させて得られ、かつ (i) 成分由来のヒドロシリル基が実質上残存した化合物であることを特徴とする、請求の範囲第 1 項に記載の硬化剤。

7. 次の式 (6) 又は式 (7) で示される構造を有することを特徴とする、請求の範囲第 1 項に記載の硬化剤。



(式 (6) 中、 $m \geq 2$ 、 $n \geq 0$ 、 $l$ 、 $k$ 、 $q \geq 1$ 、 $p$  は 0 ~ 5 の整数、 $10 \leq (m + n + l + k) \times q \leq 80$  であり、 $R^6$ 、 $R^7$  は、炭素数 0 ~ 6 の 1 価の置換基、 $R^8$  は、分子量が 100 ~ 10,000 のポリオキシアルキレン鎖を示し、 $R^9$ 、 $R^{10}$  は、水素又は炭素数 1 ~ 20 の炭化水素基を示す。 $m$  個、 $n$  個、1 個、 $k$  個の  $R^6$ 、 $n$  個、 $p$  個の  $R^7$  は、それぞれ同じものでも異なるものでもよい。X は、構成元素として C, H, N, O, S, ハロゲンのみを含む炭素数 0 ~ 10 の 2 価の置換基を示す。)



(式(7)中、 $m \geq 2$ 、 $n \geq 0$ 、 $1$ 、 $k$ 、 $q \geq 1$ 、 $p$ は $0 \sim 5$ の整数、 $3 \leq (m+n+1+k) \times q \leq 20$ であり、 $R^5$ 、 $R^7$ 、 $R^8$ 、 $X$ は、式(6)と同じ。)

8. (A) 分子中に少なくとも1個の炭素-炭素二重結合を含有する有機化合物、及び

(B) ヒドロシリル基を有する有機系硬化剤

を必須成分とし、前記(B)成分が請求の範囲第1項～第7項のいずれか1項に記載の硬化剤である硬化性組成物。

9. (C) ヒドロシリル化触媒

をさらに含有することを特徴とする、請求の範囲第8項に記載の硬化性組成物。

10. (A) 分子中に少なくとも1個の炭素-炭素二重結合を含有する有機化合物、及び

(B) ヒドロシリル基を有する有機系硬化剤

(D) 発泡剤及び／又はOH基を有する化合物、

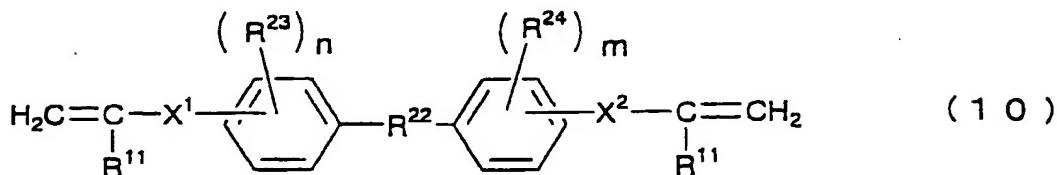
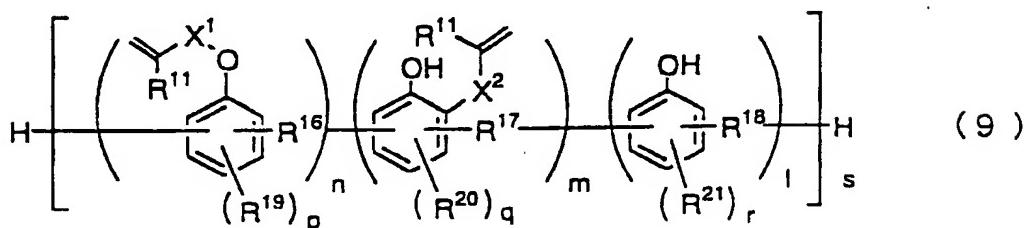
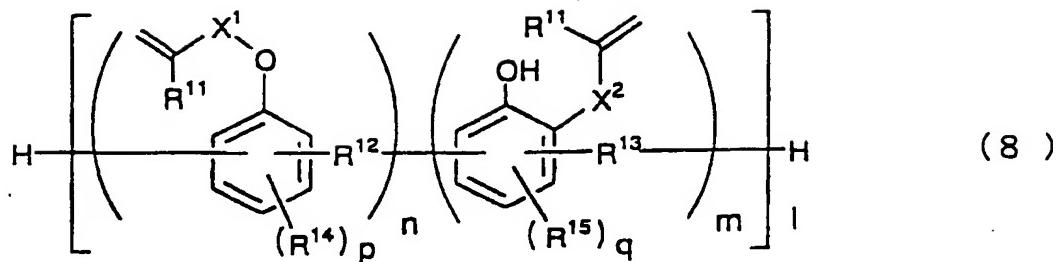
を必須成分とし、前記(B)成分が請求の範囲第1項～第7項のいずれか1項に記載の有機系硬化剤である発泡性樹脂組成物。

11. (C) ヒドロシリル化触媒

をさらに含有することを特徴とする、請求の範囲第10項に記載の硬化性組成物。

12. 前記(A)成分の有機化合物の分子骨格が、炭素、酸素、水素、窒素、イオウ、ハロゲンのうちのいずれか1種以上の元素のみからなる、請求の範囲第10項又は第11項記載の発泡性樹脂組成物。

13. 前記(A)成分の有機化合物が、下記一般式(8)～式(10)；



(式(8)～式(10)において、R<sup>11</sup>は、H又はCH<sub>3</sub>を示し、R<sup>12</sup>、R<sup>13</sup>、R<sup>16</sup>、R<sup>17</sup>、R<sup>18</sup>、R<sup>22</sup>は、炭素数0～6の2価の置換基を示し、R<sup>14</sup>、R<sup>15</sup>、R<sup>19</sup>、R<sup>20</sup>、R<sup>21</sup>、R<sup>23</sup>、R<sup>24</sup>は、炭素数0～6の1価の置換基を示し、X<sup>1</sup>、X<sup>2</sup>は、炭素数0～10の2価の置換基を示す。また、式(8)において、n、mは、0～300の整数、lは、1～300の整数、p、qは、0～3の整数を示し、式(9)において、n、m、lは、0～300の整数、sは、1～300の整数、p、q、rは、0～3の整数を示し、式(10)において、n、mは、0～4の整数を示す。)のうちのいずれか1種以上の構造を分子骨格として有する、請求の範囲第10項又は第11項記載の発泡性樹脂組成物。

14. 前記(A)成分の有機化合物の炭素-炭素二重結合の数が、1分子あたり平均2個以上であることを特徴とする、請求の範囲第10～13項

のいずれか 1 項に記載の発泡性樹脂組成物。

15. 前記 (D) 成分の発泡剤が、炭化水素、ハイドロクロロフルオロカーボン、又はハイドロフルオロカーボンから選ばれる化合物、あるいはそれらの混合物である、請求の範囲第 10 ~ 14 項のいずれか 1 項に記載の発泡性樹脂組成物。

16. 前記 (D) 成分の OH 基を有する化合物が、アルコール、カルボン酸、及び水のうちの 1 種以上からなることを特徴とする、請求の範囲第 10 ~ 15 項のいずれか 1 項に記載の発泡性樹脂組成物。

17. 請求の範囲第 10 ~ 16 項のいずれか 1 項に記載の発泡性樹脂組成物を反応させて得られる発泡体。

18. 請求の範囲第 10 ~ 16 項のいずれか 1 項に記載の発泡性樹脂組成物を常温あるいは比較的低温の加熱下において反応させ、発泡硬化させることを特徴とする発泡体の製造方法。

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/04988

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl<sup>6</sup> C08L101/00, C08L83/05, C08K5/54, C08J9/04, C08G77/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl<sup>6</sup> C08L1/00-101/14, C08K3/00-13/08, C08J9/00-9/42, C08G77/00-77/62

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926-1996 Tokoku Jitsuyo Shinan Koho 1994-1998  
Kokai Jitsuyo Shinan Koho 1971-1997

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP, 3-95266, A (Kaneka Corp.), 19 April, 1991 (19. 04. 91), Claim 9 ; page 21, Table 4 ; page 23, Example 10 ; page 24, Table 6 & US, 5409995, A & US, 5580925, A & EP, 431173, A1 & EP, 434840, A1 & DE, 69021341, A1	1 2-18
A	JP, 9-302095, A (Kaneka Corp.), 25 November, 1997 (25. 11. 97), Claims (Family: none)	1-18
PX	JP, 10-158407, A (Kaneka Corp.), 16 June, 1998 (16. 06. 98), Claim 2, page 9, Par. Nos. [0013], [0014] ; page 11, Par. No. [0019] (Family: none)	1-4, 6, 7
A	JP, 8-337670, A (Toshiba Silicone Co., Ltd.), 24 December, 1996 (24. 12. 96), Claims (Family: none)	1-18

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
5 February, 1999 (05. 02. 99)Date of mailing of the international search report  
16 February, 1999 (16. 02. 99)Name and mailing address of the ISA/  
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

## 国際調査報告

国際出願番号 PCT/JP98/04988

A. 発明の属する分野の分類（国際特許分類（IPC））  
 Int. Cl° C08L101/00, C08L83/05, C08K5/54, C08J9/04, C08G77/14

## B. 調査を行った分野

調査を行った最小限資料（国際特許分類（IPC））  
 Int. Cl° C08L1/00-101/14, C08K3/00-13/08, C08J9/00-9/42, C08G77/00-77/62

## 最小限資料以外の資料で調査を行った分野に含まれるもの

日本国実用新案公報	1926-1996年
日本国公開実用新案公報	1971-1997年
日本国登録実用新案公報	1994-1998年

## 国際調査で使用した電子データベース（データベースの名称、調査に使用した用語）

## C. 関連すると認められる文献

引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
X A	J P, 3-95266, A (鐘淵化学工業株式会社), 19. 4月. 1991 (19. 04. 91), 特許請求の範囲, 請求項9, 第21頁第4表, 第23頁実施例10、第24頁第6表 &US, 5409995, A&US, 5580925, A &EP, 431173, A1&EP, 434840, A1 &DE, 69021341, A1	1 2-18
A	J P, 9-302095, A (鐘淵化学工業株式会社), 25. 11月. 1997 (25. 11. 97), 特許請求の範囲 (ファミリーなし)	1-18

 C欄の続きにも文献が列挙されている。 パテントファミリーに関する別紙を参照。

## \* 引用文献のカテゴリー

- 「A」特に関連のある文献ではなく、一般的技術水準を示すもの
- 「E」先行文献ではあるが、国際出願日以後に公表されたもの
- 「L」優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献（理由を付す）
- 「O」口頭による開示、使用、展示等に言及する文献
- 「P」国際出願日前で、かつ優先権の主張の基礎となる出願

## の日の後に公表された文献

「T」国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの

「X」特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの

「Y」特に関連のある文献であって、当該文献と他の1以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの

「&」同一パテントファミリー文献

## 国際調査を完了した日

05. 02. 99

## 国際調査報告の発送日

16.02.99

## 国際調査機関の名称及びあて先

日本国特許庁 (ISA/JP)

郵便番号 100-8915

東京都千代田区霞が関三丁目4番3号

## 特許庁審査官（権限のある職員）

林 美穂

印

電話番号 03-3581-1101 内線 3458

C(続き) . 関連すると認められる文献		
引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
P X	J P, 10-158407, A (鐘淵化学工業株式会社), 16. 6月. 1998 (16. 06. 98), 特許請求の範囲, 請求項2、第9頁[0013], [0014], 第11頁[0019] (ファミリーなし)	1-4, 6, 7
A	J P, 8-337670, A (東芝シリコーン株式会社), 24. 12月. 1996 (24. 12. 96), 特許請求の範囲 (ファミリーなし)	1-18

## \* NOTICES \*

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

Technical field, the hardenability constituent using the organic system hardening agent and this hardening agent which contain a hydrosilyl group in this invention, and ordinary temperature — or in the bottom of low-temperature heating, it foams and hardens comparatively. Therefore, it is related with foam using the fizz resin composition generating foam and its constituent, and a manufacturing method for the same.

Background art Various kinds of things are developed as a hardenability liquid composition which hardens and generates a rubber-like substance conventionally. The polyorganosiloxane especially which has an average of two pieces or a vinyl group beyond it in an end or a chain in one molecule as a curing system excellent in depths hardenability, What constructs a bridge by the polyorgano hydrogen siloxane which has a hydrogen atom combined with a silicon atom in [ two or more ] one molecule is developed, and it is used as a sealing agent and a potting agent using the outstanding weatherability, a water resisting property, and heat resistance. However, this system has received restriction in that use from a point of being [ whose an adhesive property is / high-cost / bad ] easy to generate mold. Generally the above-mentioned polyorganosiloxane has the bad compatibility over an organic system polymer. Even if it is going to stiffen a polyorgano hydrogen siloxane and the organic polymer containing a carbon-carbon double bond (henceforth an alkene group), Hydrolysis and the dehydration condensation reaction of the polyorgano hydrogen siloxane were promoted by phase separation, and there was a problem that mechanical characteristic sufficient for void generating was not acquired.

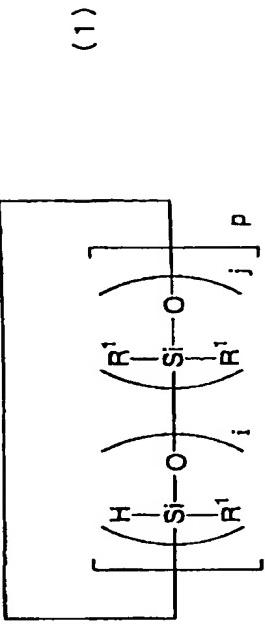
About the foaming agent used for the use of thermal insulation etc., it is required that thermal conductivity should be low as the important characteristic, and for this reason, especially to be at a rate of a high closed cell moreover in high expansion ratio is desired.

In order to solve the above mentioned problem, the organic system hardening agent which has a hydrosilyl group in a molecule is proposed (JP.3-95266.A). As generally as the organic polymer containing an alkene group, this hardening agent has good compatibility. However, this hardening agent does not have compatibility with a sufficient organic system compound which contains a polar high alkene group like a phenol system compound, for example, either. Therefore, even if it was going to stiffen these hardening agents and the organic system compound containing a polar high alkene group, there was a problem that a transparent and uniform hardened material was hard to be obtained by phase separation.

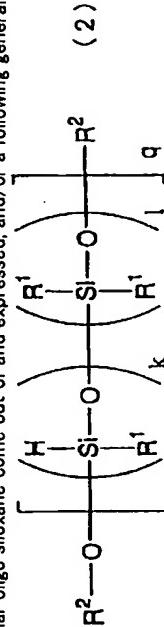
It is found out that foam with high expansion ratio is obtained by low toxicity by using as the main ingredients the compound which, on the other hand, has an organic polymer which has a carbon-carbon double bond, and a hydrosilyl group (JP.8-81594.A). However, also when obtaining foam from the compound which has an organic polymer which has the above-mentioned carbon-carbon double bond, and a hydrosilyl group. For example, when the organic system compound containing a polar high carbon-carbon double bond like a phenol system compound was used the foam compatibility with the compound which generally has a hydrosilyl group is bad, is high expansion ratio, and is [ foam ] moreover a rate of a high closed cell had the problem that it was not obtained.

This invention is made in light of the above-mentioned problems, and especially the first invention tends to provide the hardening agent in which the organic system compound containing a polar high carbon-carbon double bond has sufficient compatibility. In the second invention, the hardenability constituent which gives a hardened material with it is provided using the hardening agent concerning the first above-mentioned invention. [ high transparency and ] [ uniform ] the third invention — ordinary temperature — or foam curing being comparatively carried out under low-temperature heating, and, And it aims at providing foam using the fizz resin composition in which foam with expansion ratio high also when the organic system compound containing an especially polar high carbon-carbon double bond is used, and a rate of a closed cell high moreover is obtained, and its constituent, and a manufacturing method for the same. Indication of an invention In order to solve this technical problem, this invention persons have good compatibility with the organic compound in which the compound which has a specific structure as a result of research has at least one carbon-carbon double bond in a molecule wholeheartedly. And by using this compound as a hardening agent, it found out that each above-mentioned technical problem was solvable, and resulted in this invention. First, the hardening agent concerning the first invention shall have one of the following structures.

The first hardening agent is an organic system hardening agent which has one or more phenolic hydroxyl groups and two or more hydrosilyl groups in intramolecular, (a) following general formula (1)



(R<sup>1</sup>) expresses the basis as which a hydrogen atom and a carbon number are chosen from the organic group of the monovalence of 1-20 among a formula (1), and even if each R<sup>1</sup> is the same, it differs, and its peach is good.) It is i>=2, j>=0, and p>=1, and i, j, and p are numbers with which it is satisfied of 3 <=(i+j) xp<-50. The annular oligo siloxane come out of and expressed, and/or a following general formula (2)



a formula — ( — two — ) — inside — R — 1 — the above — the same — R<sup>2</sup> expresses the basis as which a hydrogen atom, -Si(CH<sub>3</sub>)<sub>3</sub>, -Si(CH<sub>3</sub>)<sub>2</sub>H, and a carbon number are chosen from the organic group of the monovalence of 1-20, and each R<sup>2</sup> may be the same or may differ. It is k>=2, i>=0, and q>=1, and k, l, and q are numbers with which it is satisfied of 2 <=(k+l) xq<=50. The chain polysiloxane expressed and (b) following general formula (3)

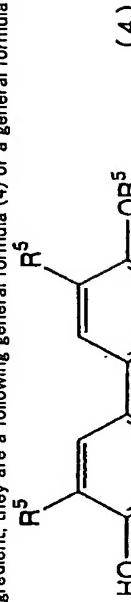


(m and n express the number of 0-2.) R<sup>3</sup> expresses the organic group of the monovalence of the carbon numbers 1-25 containing one or more alkenyl groups, and when m is two or more, each R<sup>3</sup> may be the same or may differ. R<sup>4</sup> expresses the basis of the monovalence chosen from a halogen atom, the alkoxyl group of the carbon numbers 1-6, and the organic group of the monovalence of the carbon numbers 1-25, and when p is 2, each R<sup>4</sup> may be the same or may differ.

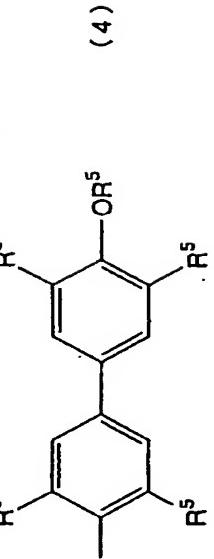
Come out, the compound which has one or more alkenyl groups and one or more phenolic hydroxyl groups is made to react to the intramolecular expressed, and it is obtained.

In the above-mentioned formula (1) and (2), it is preferred that j and/or l are 0. In that case, it is more preferred that it is a number with which it sets and said i is satisfied of 3<=i<=7, and/or said k is a number with which it is satisfied of 2<=k<=10.

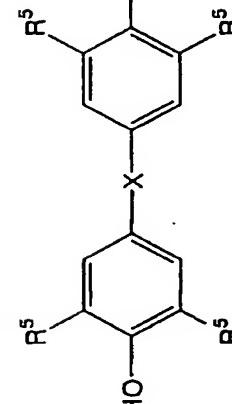
As a (b) ingredient, they are a following general formula (4) or a general formula (5).



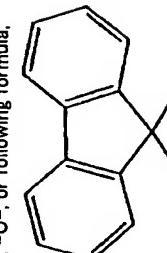
R<sup>5</sup>



R<sup>5</sup>



(R<sup>5</sup>) expresses the organic group of the monovalence of the carbon numbers 1-10 containing a hydrogen atom or one or more alkenyl groups among a formula (4) and (5), and each R<sup>5</sup> may be the same or may differ.) The inside of a formula (5) and X are -CH<sub>2</sub>-,-C(CH<sub>3</sub>)<sub>2</sub>-,-CH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-,-C(CF<sub>3</sub>)<sub>2</sub>-,-CO-, -SO<sub>2</sub>-,-O-, or following formula:



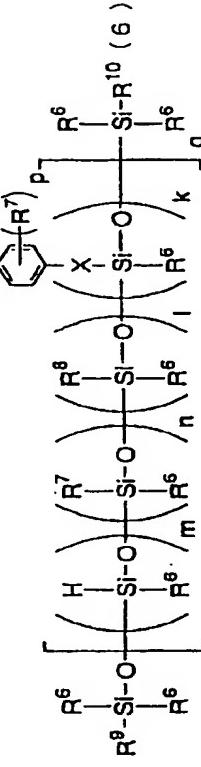
The substituent of the bivalence which comes out and is chosen from the basis expressed is shown.

It comes out and the compound which is expressed and which has one or more alkenyl groups and one or more phenolic hydroxyl groups in intramolecular is used especially suitably.

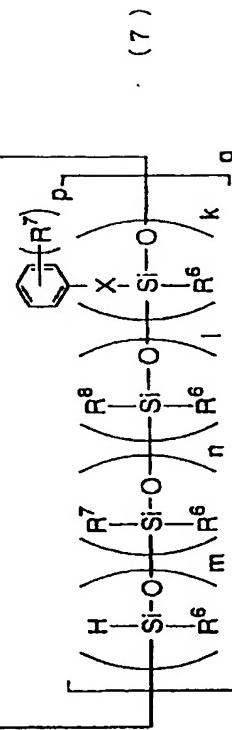
The second hardening agent concerning this invention is following ingredient (i), (ii), and (iii):

(i) The chain and/or annular ORGANO hydrogen siloxane whose number of the silicon atoms in one molecule is 3-10, (ii)(ii) the compound which has a functional group which can react to the hydroxyl group of an ingredient in [ two or more ] one molecule. (iii)(ii) it is obtained by making the organic compound which contains the functional group which can react to the hydroxyl group of an ingredient in [ one ] one molecule react, and, moreover, the hydroxyl group of (i) ingredient origin is the compound which remained on parenchyma.

The third hardening agent has the structure shown by a following formula (6) or formula (7).



(m)=2, n)=0, l, k, q)=1, and p are an integer of 0-5, and 10<=(m+n+l+k) xq<=80 among a formula (6), and R<sup>6</sup> and R<sup>7</sup> A molecular weight shows polyoxyalkylene chain of 100-10,000, and, as for the univalent substituent of the carbon numbers 0-6, and R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> show hydrogen or the hydrocarbon group of the carbon numbers 1-20. What has m pieces, n pieces, l pieces, k R<sup>6</sup>, n pieces, and p respectively the same R<sup>7</sup> may differ. X shows the divalent substituent of the carbon numbers 0-10 which contain only C, H, N, O, S, and halogen as a composing element.



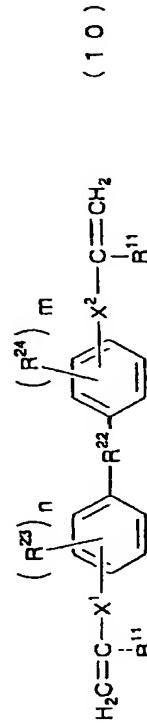
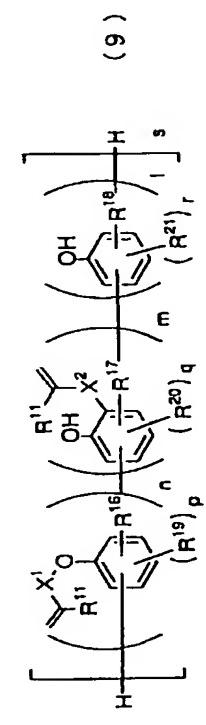
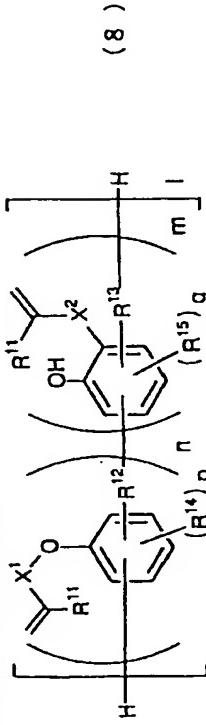
(m)>2, n)=0, l, k, q)=1, and p are an integer of 0-5, and 3<=(m+n+l+k) xq<=20 among a formula (7), and R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, and X are the same as a formula (6).)

Next, the organic compound in which the hardenability constituent concerning the second invention contains at least one carbon-carbon double bond in the (A) molecule, (B) Contain the organic system hardening agent which has a hydroxyl group as an essential ingredient, preferably, contain the (C) hydrosilylation catalyst further and contain any one sort of the organic system hardening agent of an invention of the above first, or two sorts or more as the (B) ingredient.

The fizz resin composition concerning the third invention contains further the compound which has the (D) foaming agent and/or an OH radical in addition to the above-mentioned (A) ingredient and the (B) ingredient as an essential ingredient, and contains the (C) hydrosilylation catalyst further preferably.

As for the molecular skeleton of the organic compound of the (A) ingredient in the second and third inventions, it is preferred to consist only of carbon, oxygen, hydrogen, nitrogen, sulfur, and

any one or more sorts of elements of the halogen.  
More specifically as an organic compound of the (A) ingredient, they are a following general formula (8) – a formula (10).



(R<sup>11</sup> in a formula (8) – a formula (10)) H or CH<sub>3</sub> is shown and R<sup>12</sup>, R<sup>13</sup>, R<sup>16</sup>, R<sup>17</sup>, R<sup>18</sup>, and R<sup>22</sup>. The divalent substituent of the carbon numbers 0–6 is shown, R<sup>14</sup>, R<sup>15</sup>, R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup>, R<sup>23</sup>, and R<sup>24</sup> show the univalent substituent of the carbon numbers 0–6 and X<sup>1</sup> and X<sup>2</sup> show the divalent substituent of the carbon numbers 0–10. n and m in a formula (8) the integer of 0–300 and l, The integer of 1–300, p, and q show the integer of 0–3, in a formula (9), n, m, and l show the integer of 0–300, as for the integer of 1–300, p, q, and r, s shows the integer of 0–3, and n and m show the integer of 0–4 in a formula (10).

\*\* — what has any one or more sorts of inner structures as a molecular skeleton is used suitably.

As for the carbon–carbon double bond of the organic compound of the above-mentioned (A) ingredient, it is preferred that it is an average of two or more per molecule.  
As an example of the foaming agent of the above-mentioned (D) ingredient, the compounds chosen from hydrocarbon, ether, hydrochlorofluorocarbon, or hydrofluorocarbon or those mixtures are mentioned. As an example of the compound which has an OH radical, one or more sorts in alcohol, carboxylic acid, and water are mentioned.

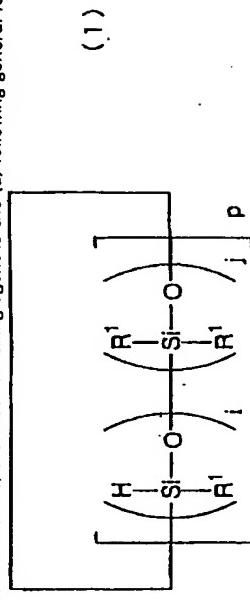
Ordinary temperature or by carrying out foam curing under low-temperature heating comparatively, foam with high expansion ratio and a rate of a closed cell high moreover is obtained in the above-mentioned fizz resin composition. The best result for inventing The above-mentioned first – the third invention are explained in detail hereafter.

1. Hardening agent The hardening agent concerning the first invention is characterized by compatibility with the organic compound which contains at least one carbon–carbon double bond in a molecule being good. Here, the “organic compound” refers to the compound which does not include a siloxane bond substantially in a molecular skeleton, when the agitation mix of it is carried out to “compatibility is good”, with the above-mentioned organic compound, it shall dissolve in a uniform state, and it shall refer to neither nebula nor phase separation being

accepted by observation by a naked eye. Or it shall say that neither nebula nor phase separation is accepted even if it carries out for [ 10 minutes ] grade centrifugal separation by 1000 revolutions per minute after an agitation mix.

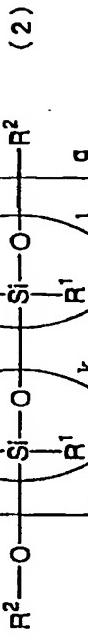
The hardened material obtained by compatibility being good using this becomes the thing excellent in appearance, such as a mechanical property and transparency, and the rate of a closed cell of foam is high, and it becomes what was excellent in insulation efficiency etc. as a result.  
As the concrete structure, the first hardening agent is the (a) following general formula (1).

(1)



The annular oligo siloxane and/or following general formula (2) with which it is come out and expressed

(2)



The chain polysiloxane come out of and expressed, and the (b) following general formula (3)



(m and n express the number of 1–3 independently among a formula (3), respectively, and p expresses the number of 0–2.) R<sup>3</sup> expresses the organic group of the monovalence of the carbon numbers 1–25 containing one or more alkenyl groups, and when m is two or more, each R<sup>3</sup> may be the same or may differ. R<sup>4</sup> expresses the basis of the monovalence chosen from a halogen atom, the alkoxy group of the carbon numbers 1–6, and the organic group of the monovalence of the carbon numbers 1–25, and when p is 2, each R<sup>4</sup> may be the same or may differ. It is a compound which comes out, makes the compound which has one or more alketyl groups and one or more phenolic hydroxyl groups react to the intramolecular expressed, and is obtained.

R<sup>1</sup> of a chain polysiloxane expressed with the annular polysiloxane and general formula (2) which are expressed with the above-mentioned general formula (1) is a basis as which a hydrogen field and a carbon number are chosen from the organic group of the monovalence of 1–20. As an example of the organic group of monovalence, an alkyl group, an alkoxy group, an alkyl halide group, an alkyl group, a cycloalkyl group, an alkenyl group, a cycloalkenyl group, or an aryl group is mentioned.

The substituted alkyl group expressed with a trifluoropropyl group, a methyl group, an ethyl

group, and  $-CH_2CH_2R$  among these (R here) A halogen atom, a cyano group, a phenyl group, an alkoxy group, an alkyl carbonyl group, the organic group of monovalence, such as an alkoxycarbonyl group, is expressed — the substituted alkyl group (R here) expressed with  $-CH_2CH(CH_3)R$  the organic group of monovalence such as a halogen atom, a phenyl group, an alkyl carbonyl group, and an alkoxycarbonyl group, is expressed — the substituted alkyl group (R here expresses the organic group of monovalence, such as a halogen atom, a hydroxyl group, and an alkoxy group,) and phenyl group which are expressed with  $CH_2CH_2CH_2R$  — industrial general — acquisition — it is desirable from an easy thing and a point of chemical stability.

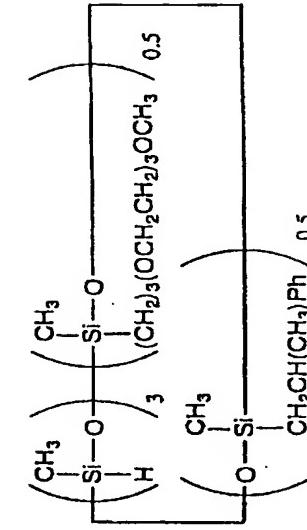
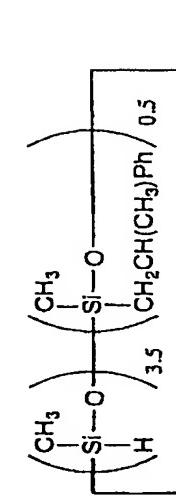
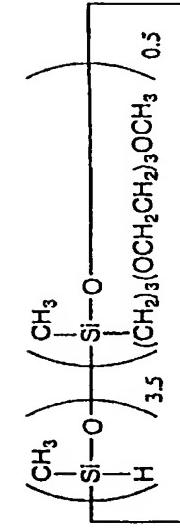
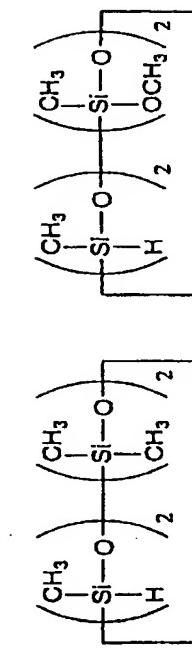
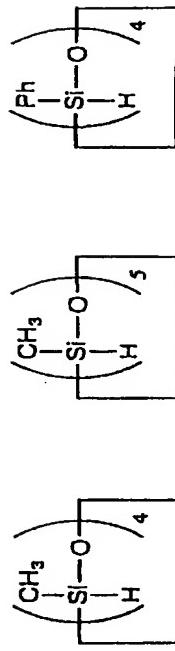
Among these A methyl group, a trifluoropropyl group, a phenyl group, 2-phenylethyl group, Or the substituted alkyl group expressed with  $-CH_2CH_2CH_2(OCH_2CH_2)_nOCH_3$  (n Here expresses 0 or 20 or less positive number.) is still more preferred, and a methyl group is the most preferred. Each R may be the same or may differ.

$R^2$  of a chain polysiloxane expressed with said general formula (2) is a hydrogen atom,  $-Si(CH_3)_3$   $-Si(CH_3)_2H$ , and a basis as which a carbon number is chosen from the organic group of the monovalence of 1~20.

As an example of the organic group of monovalence, a methyl group, an ethyl group, a propyl group, a butyl group, a phenyl group, or the substituted alkyl group expressed with  $-(CH_2CH_2O)$   $nCH_3$  (n here expresses 0 or 20 or less positive number) is mentioned.

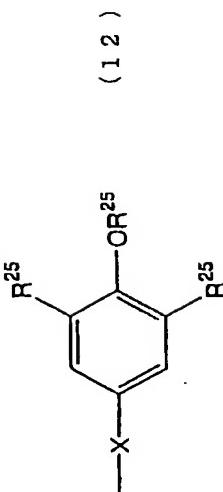
i of an annular polysiloxane expressed with said general formula (1), j, p, and k of a chain polysiloxane expressed with said general formula (2). As for two or more numbers and j, 0 or a positive number, and p of i are one or more numbers among l and q. And i, j, and p are numbers with which it is satisfied of  $3 \leq (i+j)xp \leq 50$ . Although 0 or a positive number, and q of k are one or more numbers as for two or more numbers and l and k and l should just be numbers with which it is satisfied of  $2 \leq (k+l)xq \leq 50$ , it is industrially preferred that acquisition is generally  $j=0$  from an easy point. The hardening agent obtained deals with it by hypoviscosity, and it is preferred from points, like a sex is good that it is  $3 \leq i \leq 7$  and/or  $2 \leq k \leq 10$ .

As an example of an annular polysiloxane expressed with said general formula (1), it is a following formula.:

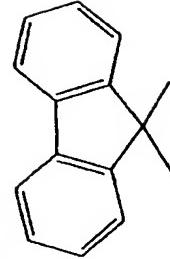


It comes out and the compound expressed is mentioned.  
As an example of a chain polysiloxane expressed with said general formula (2), it is a formula.





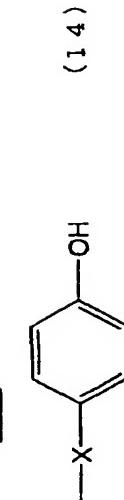
(R<sup>25</sup> is a hydrogen atom or an allyl group among a formula (11) and (12), and at least one R<sup>25</sup> is an allyl group.) The inside of a formula (12) and X are -CH<sub>2</sub><sup>-</sup>, -C(CH<sub>3</sub>)<sub>2</sub><sup>-</sup>, -CH(CH<sub>3</sub>)<sup>-</sup>, -C(F<sub>3</sub>)<sub>2</sub><sup>-</sup>, -CO<sup>-</sup>, -SO<sub>2</sub><sup>-</sup>, -O<sup>-</sup>, or a formula :  
2 : -CO<sub>2</sub><sup>-</sup>, -SO<sub>2</sub><sup>-</sup>, -O<sup>-</sup>, or a formula :.



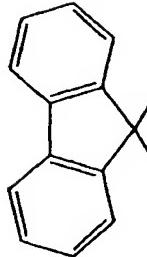
It is a basis come out of and expressed.

It comes out and the basis expressed is mentioned.  
Reactivity with industrially available [ among these / generally ] in the basis expressed with an allyl group or the above-mentioned general formula (11) or (12) or a hydroxyl group is preferred from a good thing.

as the example of R<sup>4</sup> of a compound which has one or more alketyl groups and one or more phenolic hydroxyl groups in the intramolecular expressed with the above-mentioned general formula (3) — a chlorine atom, a methoxy group, a methyl group, a hydroxy carbonyl group, an alkoxycarbonyl group, or a following general formula (13) — or (14)

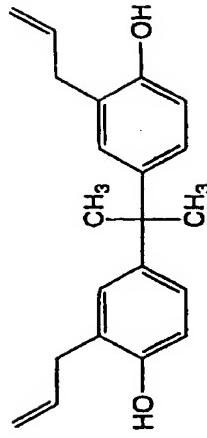
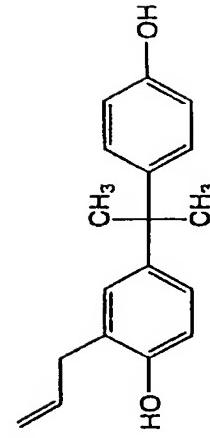
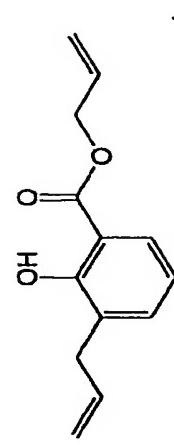
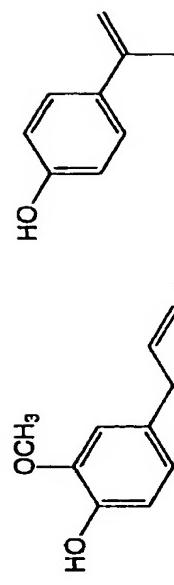
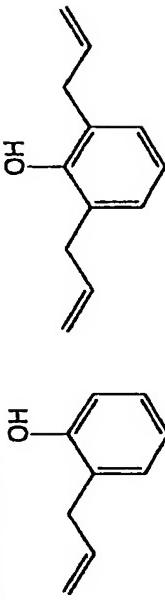


(The inside of a formula (14) and X are -CH<sub>2</sub><sup>-</sup> and -C(CH<sub>3</sub>)<sub>2</sub><sup>-</sup>, -CH(CH<sub>3</sub>)<sup>-</sup>, -C(OF<sub>3</sub>)<sub>2</sub><sup>-</sup>, -CO<sup>-</sup>, -SO<sub>2</sub><sup>-</sup>, -O<sup>-</sup>, or formula :.)

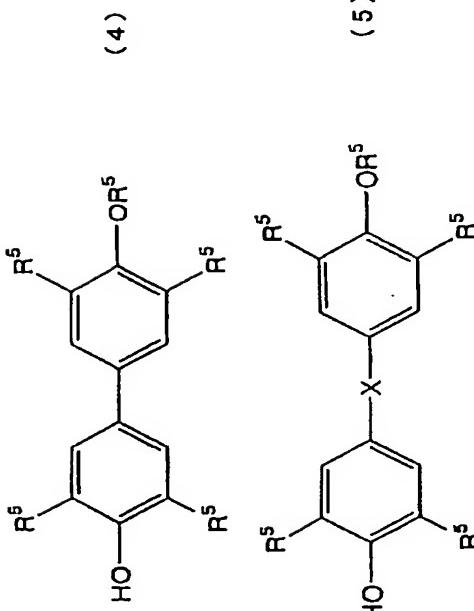


It comes out and the basis expressed is shown.  
It comes out and the basis expressed is mentioned.  
The basis expressed with a methoxy group or the above-mentioned general formula (13) or (14) among these is preferred from industrially available generally. When these two or more

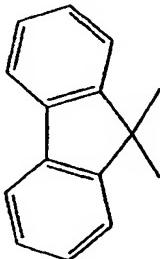
substituents have replaced, it may be the same respectively or may differ.  
As an example of a compound of having one or more alketyl groups and one or more Feni Nord nature hydroxyl groups in the intramolecular expressed with the above-mentioned general formula (3), it is a formula:



It comes out and the compound expressed is mentioned.  
although the (b) ingredient was described above — inside — a following general formula (4) — or (5)



(R<sup>5</sup>) expresses the organic group of the monovalence of the carbon numbers 1-10 containing a hydrogen atom or one or more alkenyl groups among a formula (4) and (5), and each R<sup>5</sup> may be the same or may differ.) Or -CH<sub>2</sub><sup>-</sup>, -C(CH<sub>3</sub>)<sup>2</sup><sup>-</sup>, -CH(CH<sub>3</sub>)<sup>-</sup>, -C(GF<sub>3</sub>)<sup>2</sup><sup>-</sup>, -CO<sup>-</sup>, -SO<sub>2</sub><sup>-</sup>, -O<sup>-</sup>, or a formula:



The substituent of the bivalence which comes out and is chosen from the basis expressed is shown.

It comes out and the compound which is expressed and which has one or more alkenyl groups and one or more phenolic hydroxyl groups in intramolecular is used suitably.

Although the hardening agent of this invention can be obtained by the ability to make the above-mentioned (a) ingredient and the (b) ingredient able to react. As an example of a hydrosilylation catalyst in which it is used in that case, The thing which made carriers, such as a simple substance of platinum, alumina, silica, and carbon black, support solid platinum, A complex with chloroplatinic acid, chloroplatinic acid, alcohol, aldehyde, ketone, etc., Platinum-olefin complex (for example, it Pt(CH<sub>2</sub>=CH<sub>2</sub>)<sup>3</sup>(PPh<sub>3</sub>)<sup>2</sup> and) Pt(CH<sub>2</sub>=CH<sub>2</sub>)<sup>2</sup>C<sub>12</sub>: Platinum-vinyl siloxane complex (for example, it Pt(VMe<sub>2</sub>-SiOSiMe<sub>2</sub>, Vi)<sub>n</sub> and) Pt[(MeViSiO)<sub>4</sub>]<sub>n</sub>: a platinum-phosphine complex. (For example, Pt(PPh<sub>3</sub>)<sub>4</sub>, Pt(PBu<sub>3</sub>)<sub>4</sub>), a platinum-phosphite complex (for example, Pt[P(OPh)<sub>3</sub>]<sub>4</sub>) [ and ] Pt[POBu]<sub>3</sub> ]<sup>4</sup> (among a formula, a methyl group and Bu express a butyl group, Ph expresses a vinyl group, Ph expresses a phenyl group as for Me, and n and m express an integer.), dicarbonyl dichloroplatinum, and a carb SHUTETO (Karstedt) catalyst. The platinum alcoholate catalyst indicated in the platinum-hydrocarbon complex indicated in U.S. Pat. No. 3159601 of Ashby (Ashby) and the No. 3159662 specification and the U.S. Pat. No. 3220972 specification of RAMORO (Lamoreau) is mentioned. The platinum chloride-olefin complex indicated in the U.S. Pat. No. 3516946 specification of Modic (Modic) is also useful in this invention. As an example of catalysts other than a platinum compound, RhCl(PPh<sub>3</sub>)<sub>3</sub>, RhCl<sub>3</sub>,

Rh/aluminum<sub>2</sub>O<sub>3</sub>, RuCl<sub>3</sub>, FeCl<sub>3</sub>, AlCl<sub>3</sub>, PdCl<sub>2</sub> and 2H<sub>2</sub>O, NiCl<sub>2</sub>, TiCl<sub>4</sub>, etc. are mentioned. In these, chloroplatinic acid, a platinum-olefin complex, a platinum-vinyl siloxane complex, etc. are preferred from a point of catalytic activity. These catalysts may be used alone and may be used together two or more sorts.

Although the addition in particular of a catalyst is not limited, its range of a 10<sup>-1</sup> – 10<sup>-8</sup> mol is preferred to hydrosilyl group 1 mol, and it is the range of a 10<sup>-2</sup> – 10<sup>-6</sup> mol more preferably. A phosphine system compound and a phosphine complex can be used as a co-catalyst with the above-mentioned catalyst. As such a phosphine system compound, they are triphenyl phosphine, PMe<sub>3</sub>, PEt<sub>3</sub>, and PPt<sub>3</sub> (here, Pr expresses a propyl group.) It is the same as that of the following. Although there are P(n-Bu)<sub>3</sub>, P(cyclo-C<sub>6</sub>H<sub>4</sub>M<sub>6</sub>)<sub>3</sub>, P(o-C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>, etc., it is not limited to these. As a phosphine complex, for example Cr(CO)<sub>5</sub>PPh<sub>3</sub>, Cr(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> (Sis and trans isomer), Cr(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub> (fac and mer isomer), Mo of these Cr compounds and V analog, Fe(CO)<sub>4</sub>PPh<sub>3</sub>, Ru and Os analog of Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> and these Fe compounds, CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (Sis and trans isomer), There are RhCl(CO)(PPh<sub>3</sub>)<sub>3</sub>, IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, and ClAu (PPh<sub>3</sub>). Metal complexes, such as a complex of the above-mentioned metal containing phosphines other than triphenyl phosphine, can also serve as an effective co-catalyst. The complex containing stibines, such as arsines, such as phosphite, such as P(OPh)<sub>3</sub>, and AsPh<sub>3</sub>, and SbPh<sub>3</sub>, can also serve as an effective co-catalyst.

Although the addition in particular of a co-catalyst is not limited, its range of 10<sup>-2</sup> – 10<sup>-2</sup> mol is preferred to 1 mol of catalysts, and it is the range of 10<sup>-1</sup> – 10<sup>-1</sup> mol more preferably. In a hydrosilylation reaction, although use in particular of a solvent is not needed, A first train raw material etc. are the things of a solid or hyperviscosity, and using an inactive organic solvent suitably, in following difficulty on operation of churning etc. does not interfere. To this, aromatic hydrocarbons solvents, such as benzene, toluene, and xylene, Aliphatic hydrocarbons, such as hexane and octane, ethyl ether, butyl ether, Ester solvents, such as halogenated hydrocarbon solvents, such as ketones, such as ethers solvents, such as a tetrahydrofuran, and methyl ethyl ketone, chloroform, a methylene chloride, and trichloroethylene, and ethyl acetate, etc. are illustrated. Although the quantity in particular of the solvent to be used is not limited, 100 or less weight sections are preferably used to total amount 100 weight section of the reacting agent used from a point of economical efficiency.

About the addition method of (a), (b) both ingredients, and a hydrosilylation catalyst used for this invention. Although the method of adding the (b) ingredient to the method of teaching three ingredients collectively, the method of adding the (a) ingredient and a hydrosilylation catalyst for the (b) ingredient, the (a) ingredient, and a hydrosilylation catalyst, the method of adding the (a) ingredient to the (b) ingredient and a catalyst, the method of adding each ingredient simultaneously, etc. can be considered. There is no restriction in particular. However, in order to make it react so that it may remain even after a hydrosilyl group's reacting.

(a) Since it is thought desirable for the multivalent hydrogen silicon compound which is an ingredient to always exist superfluously to the (b) ingredient, (b) The method of adding what mixed the hydrosilylation catalyst with the organic compound containing the alkenyl group which is an ingredient to the multivalent hydrogen silicon compound which the (a) ingredient is preferred.

(a) What is necessary is just to set up the mixture ratio of an ingredient and the (b) ingredient so that a hydrosilyl group may become superfluous by the mole ratio of a hydrosilyl group and an alkenyl group. It is preferred from a point of hardenability when using it as a hardening agent to set up so that a number of hydrosilyl groups which exceed one piece on an average in one molecule of the hardening agent obtained preferably may remain. After the hardening agent of this invention makes the (b) ingredient react to the superfluous (a) ingredient, it can be obtained also by the way, distillation, adsorption, precipitate, extraction, etc. remove the unreacted (a) ingredient.

50–150 \*\* of reaction temperature of 0–200 \*\* is preferably good. If reaction temperature is lower than 0 \*\*, catalytic activity will not be enough, therefore reaction velocity will become slow. If it becomes higher than 150 \*\*, a catalyst will be deactivated in many cases.

Since a transition metal catalyst exists in a hardening agent depending on an unreacted hydroxyl group and case when the hardening agent of this invention is obtained at the reaction of the (a) ingredient and the (b) ingredient. When the water in a system reacts to hydroxyl groups or a hydroxyl group gradually during a retention period, increase and gelling of viscosity may be caused.

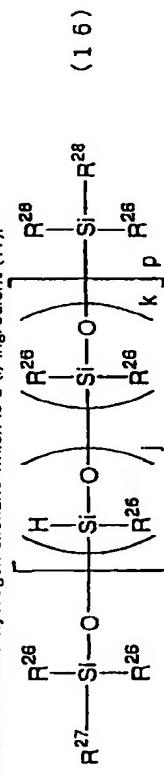
In order to avoid this, after compounding a hardening agent by a hydrosilylation reaction, the additive agent aiming at inactivation of a catalyst may be added. As an example of the additive agent used, acetylene alcohol, such as dimethylmalate, benzothiazole, and a 2-hydroxy-2-methyl-1-butyne, is mentioned. Although the quantity in particular of the additive agent to be used is not limited, its range of 1 – 10<sup>2</sup> mol is preferred to 1 mol of catalysts used for the reaction from the point of reconciling storage stability and the hardenability of a hardening agent, and the range of it is 1–30 mol more preferably.

Or in order to avoid the above-mentioned problem, a hydrosilylation catalyst may be removed from a hardening agent. As a removing method, the method of rinsing a reaction solution in silica, silica gel, alumina, ion-exchange resin, activated carbon, etc. stirring processing and the method of carrying out column processing, or neutral thru/or weak acidic solution, etc. are illustrated.

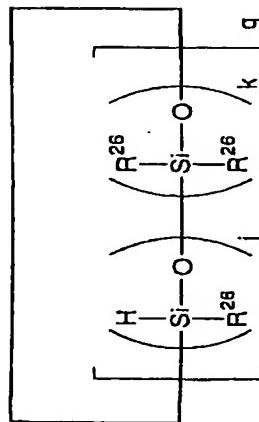
The second hardening agent is the following (i), (ii), and a (iii) ingredient:

(i) The compound in which the number of the silicon atoms in one molecule has a functional group which can react to the hydroxyl group of the chain and/or annular ORGANO hydrogen siloxane (ii) ingredient whose number is 3–10 in [ two or more ] one molecule, (iii)(i) being obtained by reacting the organic compound which contains the functional group which can react to the hydroxyl group of an ingredient in [ one ] one molecule — moreover (the hydroxyl group of (i) ingredient origin is the compound which remained on parenchyma.)

General formula [ following ] (16) Reach as a concrete example of the above-mentioned a chain or annular ORGANO hydrogen siloxane which is a (i) ingredient (17).



(It is  $j=2$ ,  $k=0$ ,  $p=1$ , and  $3 < j+k$   $x p < 8$  among a formula (16), and a hydrogen atom and a carbon number may express the basis chosen from the univalent organic group of 1–20, and  $R^{26}$  may contain one or more aromatic substitution groups.) Each  $R^{26}$  may be the same or may differ.



(It is  $j=2$ ,  $k=0$ ,  $q=1$ , and  $3 < j+k$   $x q < 10$  among a formula (17), and a hydrogen atom and a carbon number may express the basis chosen from the univalent organic group of 1–20, and  $R^{26}$

may contain one or more aromatic substitution groups.) Each  $R^{26}$  may be the same or may differ.

It comes out and what is expressed is mentioned.

As for the number of this chain and the hydroxyl groups per one molecule of cyclosiloxane, it is preferred that they are [ two or more piece ] ten or less pieces, and it is two or more pieces [ six or less ] more preferably. If the physical intensity of the foam eventually obtained as the hydroxyl group per molecule is less than two pieces falls, contraction becomes is hard to be controlled as a result and ten pieces are exceeded conversely, not only contraction but foam may be cracked.

As a more concrete example of the above-mentioned (i) ingredient, poly methyl/hydrosilsiloxane, A polyethyl hydrogen siloxane, a polypheny hydrogen siloxane, etc., 1,3,5-trimethyl cyclotetrasiloxane, 1,3,5,7-tetramethyl cyclotetrasiloxane, 1,3,5,7,9-pentamethyl cyclopentasiloxane, these mixtures, etc. are mentioned.

Next, the compound which contains the functional group which can react to the hydroxyl group of the (i) ingredient which is a (ii) ingredient in [ two or more ] a molecule is described.

(ii) As a functional group which can react to the hydroxyl group of an ingredient, the compound which has carbon–carbon double bonds, such as a vinyl group, an allyl group, an acrylic group, and an methacrylic group, an OH radical, a carboxyl group, etc. is mentioned, and these two or more sorts may exist in 1 intramolecular.

Although a carbon–carbon double bond may exist anywhere in intramolecular, it is preferred to exist in a side chain or an end from a reactant point. As for the number of the functional groups which can react to the hydroxyl group in one molecule, two or more pieces [ four or less ] are preferred, and its two or more pieces [ three or less ] are more preferred. If the number of the functional groups which can react to the hydroxyl group in one molecule exceeds four pieces, it may become gel in the case of the reaction of a (i) ingredient and a (ii) ingredient, and is not desirable.

(ii) There is no restriction in particular about the skeleton of an ingredient, and inorganic compounds, such as the usual organic monomer skeleton or an organic polymer skeleton, and water, are mentioned.

As an organic monomer skeleton, a hydrocarbon system, an aromatic hydrocarbon system, a phenol system, a bisphenol system, an epoxy resin monomer, isocyanate, or these mixtures are mentioned, for example. In an organic polymer, a polyether system, a polyester system, a polycarbonate system. Skeletons, such as a saturated hydrocarbon system, a polycrylic ester system, a polyamide system, a diallyl phthalate system, a phenolformaldahyde system (phenol resin system), a polyurethane system, a poly urea system, a melamine system polymer, and an epoxy resin, are mentioned.

As a concrete example of an ingredient, (ii) alpha, such as 1,9-decadiene, omega-alkadiene, Divinylbenzene, diarylbenzene, 1,4-butanediol, and allyl ether, Phthalic anhydride and its allyl ester, O,O'-diarylbisphenol A, 2,2-diarylbisphenol A, ethylene glycol or diethylene glycols, and these allyl ether. The allyl ester of allyl end polypropylene oxide and polyethylene oxide, a phthalic anhydride–ethylene glycol polymer, or a phthalic anhydride–diethylene–glycol polymer, a 9-decene 1–oar, ethylene glycol monoallyl ether, etc. are mentioned.

(ii) Although the molecular weight in particular of an ingredient is not limited, a 100,000 or less-about thing can use it suitably, and 10,000 or less thing is preferred.

Next, the organic compound which contains the functional group which can react to the hydroxyl group of the (i) ingredient which is a (iii) ingredient in [ one ] a molecule is described.

(iii) As a functional group which can react to the hydroxyl group of an ingredient, the compound which has carbon–carbon double bonds, such as a vinyl group, an allyl group, an acrylic group, and an methacrylic group, an OH radical, a carboxyl group, etc. is mentioned.

Although a carbon–carbon double bond may exist anywhere in intramolecular, it is preferred to exist in a side chain or an end from a reactant point.

(iii) As a skeleton of an ingredient, an organic monomer, an organic polymer, etc. quoted as a skeleton of a (ii) ingredient are illustrated.

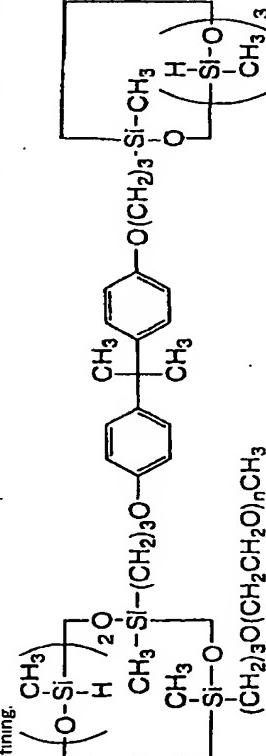
As a concrete example of an ingredient, (iii) 1-hexene, 1-octene, Alpha olefins, such as 1-decene, and 1-propanol, 1-octanol, Carboxylic acid, such as alcohols, such as ethylene glycol monoethyl ether, and 2-ethylhexanoic acid. Acrylics (meta), such as butyl acrylate and methyl methacrylate, styrene, 4-methylstyrene, 2,4-dimethylstyrene, alpha-methylstyrene, 4-bromostyrene, 2-vinylnaphthalene, allylbenzene, an allylanisole, Aromatic system compounds, such as allylphenyl ether, o-allylphenol, and p-isopropenylphenol, Polyoxalkylene, polyester, an acrylic polymer, etc. in which the piece end was replaced by the allyl group, the OH radical, the acrylic group (meta), the carboxyl group, and the organic group to which other ends do not react to a hydroxyl group are mentioned.

(iii) Although the molecular weight in particular of an ingredient is not limited, a 100,000 or less-about thing can use it suitably, and 10,000 or less thing is preferred. The mixture ratio of above-mentioned (i), (ii), and (iii) each ingredient, i.e., the number of mols of the hydroxyl group of a (i) ingredient, x, (ii) Although there is no restriction in particular about y/x at the time of setting to z the number of mols of the functional group which can react to the (i) ingredient of an ingredient, and the value of z/x, it is preferred that it is 0.01<=z/x<=0.5 and 0.001<=z/x<=0.8, and it is more preferred that it is 0.1<=z/x<=0.4 and 0.01<=z/x<=0.4.

If y/x is smaller than 0.01, compatibility is not enough, and since the viscosity rise accompanying polymers quantification etc., etc. will take place in the reaction time of a (i) ingredient and a (ii) ingredient if 0.5 is exceeded conversely, it is not desirable. If the compatibility of a system is not enough if z/x is smaller than 0.001, tendencies, like the cell of foam is ruined as a result come to be shown and 0.8 is exceeded conversely, the tendency for the effect which controls the contraction which is the purpose of this invention to decrease will arise.

In order to make (i), (ii), and a (iii) ingredient react, respectively, the above-mentioned hydrolysis catalyst etc. can be used suitably.

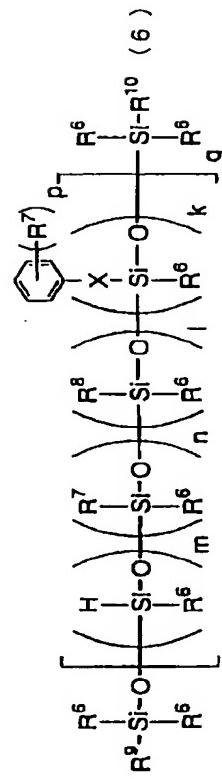
Since (ii) ingredients are many organic functions, the compound produced by making the above-mentioned (i) ingredient, a (ii) ingredient, and a (iii) ingredient react turns into a mixture of what has various structures, but the mixture which contains the compound expressed with a following formula as the one example is mentioned. These mixtures can be used as they are, without refining.



(n shows 40 or less integer preferably 100 or less [ 1 or more ] among a formula.)

When the above-mentioned first and the second hardening agent use this for a fizz resin composition, the effect that there is especially little contraction after the end of foaming is acquired.

Next, the polyorganohydrogen siloxane which denaturalized by polyoxalkylene chain and the aromatic content organic group which are the third hardening agent is described. The third hardening agent is a compound which has the structure shown by a following formula (6) or formula (7).



As a concrete example of an ingredient, (iii) 1-hexene, 1-octene, Alpha olefins, such as 1-decene, and 1-propanol, 1-octanol, Carboxylic acid, such as alcohols, such as ethylene glycol monoethyl ether, and 2-ethylhexanoic acid. Acrylics (meta), such as butyl acrylate and methyl methacrylate, styrene, 4-methylstyrene, 2,4-dimethylstyrene, alpha-methylstyrene, 4-bromostyrene, 2-vinylnaphthalene, allylbenzene, an allylanisole, Aromatic system compounds, such as allylphenyl ether, o-allylphenol, and p-isopropenylphenol, Polyoxalkylene, polyester, an acrylic polymer, etc. in which the piece end was replaced by the allyl group, the OH radical, the acrylic group (meta), the carboxyl group, and the organic group to which other ends do not react to a hydroxyl group are mentioned.

(iii) Although the molecular weight in particular of an ingredient is not limited, a 100,000 or less-about thing can use it suitably, and 10,000 or less thing is preferred.

The mixture ratio of above-mentioned (i), (ii), and (iii) each ingredient, i.e., the number of mols of the hydroxyl group of a (i) ingredient, x, (ii) Although there is no restriction in particular about y/x at the time of setting to z the number of mols of the functional group which can react to the (i) ingredient of an ingredient, and the value of z/x, it is preferred that it is 0.01<=z/x<=0.5 and 0.001<=z/x<=0.8, and it is more preferred that it is 0.1<=z/x<=0.4 and 0.01<=z/x<=0.4.

If y/x is smaller than 0.01, compatibility is not enough, and since the viscosity rise accompanying

polymers quantification etc., etc. will take place in the reaction time of a (i) ingredient and a (ii) ingredient if 0.5 is exceeded conversely, it is not desirable. If the compatibility of a system is not enough if z/x is smaller than 0.001, tendencies, like the cell of foam is ruined as a result come to be shown and 0.8 is exceeded conversely, the tendency for the effect which controls the contraction which is the purpose of this invention to decrease will arise.

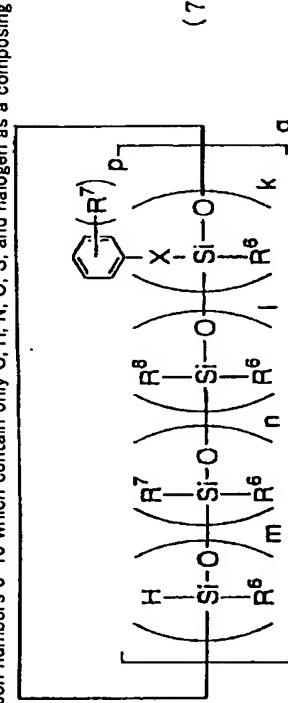
In order to make (i), (ii), and a (iii) ingredient react, respectively, the above-mentioned

hydrolysis catalyst etc. can be used suitably.

Since (ii) ingredients are many organic functions, the compound produced by making the above-mentioned (i) ingredient, a (ii) ingredient, and a (iii) ingredient react turns into a mixture of what has various structures, but the mixture which contains the compound expressed with a following formula as the one example is mentioned. These mixtures can be used as they are, without

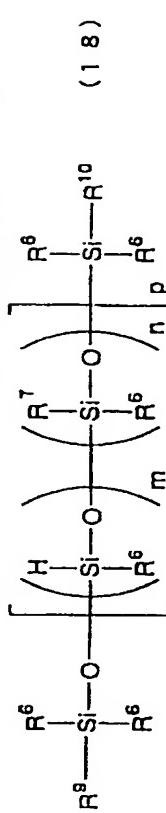
refining.

(m>2, n>0, l, k, q>1, and p are an integer of 0-5, and 10<=(m+n+l+k) xq<=80 among a formula (6), and R6 and R7) A molecular weight shows polyoxalkylene chain of 100-10,000, and, as for the univalent substituent of the carbon numbers 0-6, and R8, R9 and R10 show hydrogen or the hydrocarbon group of the carbon numbers 1-20. What has m pieces, n pieces, l pieces, k R6, n pieces, and p respectively the same R7 may differ. X shows the divalent substituent of the carbon numbers 0-10 which contain only C, H, N, O, S, and halogen as a composing element.



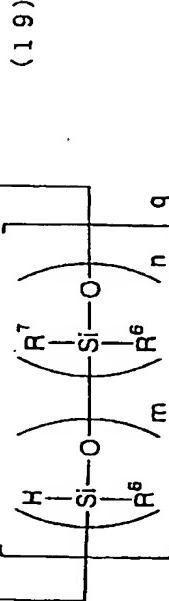
(m>2, n>0, l, k, q>1, and p are an integer of 0-5, and 10<=(m+n+l+k) xq<=80 among a formula (7), and R6, R7, R8, and R9 are the same as a formula (6).)

As a method of obtaining the polyorganohydrogen siloxane shown by the above-mentioned formula (6) or a formula (7), The polyoxalkylene compound and aromatic ring content organic group which have at the end a functional group which can react to hydrosilyl groups, such as a double bond (for example, allyl group) and an OH group. The method by a reaction with a polyorganohydrogen siloxane, and the method of compounding a polyoxalkylene chain and an aromatic ring content organic group beforehand. Or the redistribution reaction of the above-mentioned silicon compound and polyorganosiloxane, etc. can be used. Specifically, it is a following formula (18) and formula, for example (19):



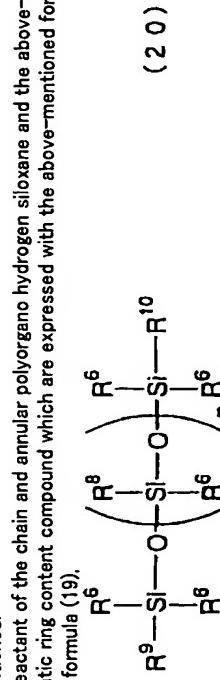
It is m>2, n>0, p>1, and 10<=(m+n) xp<=80 among (formula (18), and R6, R7, R8, and R10 are the same as the above.)

(19)

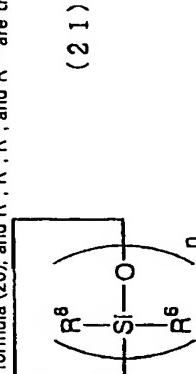


(It is  $m=2$ ,  $n=0$ ,  $q=1$ , and  $3 \leq (m+n) \times q \leq 20$  among a formula (19), and  $R^6$  and  $R^7$  are the same

as the above.) The chain and annular poly(organohydrogen siloxane come out of and expressed,  $H_2C=CHCH_2-[$   $(PO) n-(EO) m]-OH$   $H_2C=CHCH_2-2-[[(PO) n-(EO) m] I-OCH_3H_2C=CHCH_2-[(PO) n-(EO) m] I-OC_2H_5H_2C=CHCH_2-[(PO) n-(EO) m]-OC_2H_5H_2C=CHCH_2-[(PO) n-(EO) m] I-$   $OC_4H_9H_2C=CHCH_2-[(PO) n-(EO) m] I-OPh$ .  $HO-[$   $(PO) n-(EO) m]-CH_3HO-[$   $(PO) n-(EO)$   $m] I-C_2H_5-HO-[(PO) n-(EO) m] I-C_3H_7HO-[(PO) n-(EO) m] I-O_4H_gHO-[(PO) n-(EO) m] I-Ph$  (in each above-mentioned formula) Polyether system compounds, such as  $1<=(m+n) x<=80$ ,  $m-n=0$ , and  $I>=1$ . Styrene, 4-methylstyrene, alpha-methylstyrene, 4-bromostyrene, 2-vinylnaphthalene, allylbenzene, an allylanisole, A reaction with aromatic ring content compounds, such as allylphenyl ether, o-allylphenol, p-isopropenylphenol, phenol, o-cresol, benzyl alcohol, phenethyl alcohol, benzoic acid, and 4-hydronium pheasant benzoic acid, is mentioned.



(It is  $\Sigma_{i=1}^{m-1} \theta_i$  according to formula (20) and  $\theta_6 \theta_8 \theta_9$  and  $\theta_{10}$  are the same as those above.) But



(It is  $3 \leq n \leq 20$  among a formula (21), and  $R^6$  and  $R^8$  are the same as the above.)

Redistribution with \*\*, a equilibration reaction, etc. are mentioned.

As a concrete example of a polyorgano hydrogen siloxane expressed with a formula (18), Poly methylhydrogensiloxane, a polyethyl HAIDOROJIE siloxane, A polyphenyl hydrogen siloxane, a methylhydrogensiloxane dimethylsiloxane copolymer, A methylhydrogensiloxane diethyl siloxane copolymer, a methylhydrogensiloxane methylphenyl siloxane copolymer, an ethyl hydrogen

siloxane dimethylsiloxane copolymer, etc. are mentioned.

Methylhydrogensiloxane, an ethyl hydro-ROJEN siloxane, a phenyl hydrogen siloxane, dimethylsiloxane, a diethyl siloxane, a methylphenyl siloxane, etc. are mentioned, and what these carried out copolymerization and accomplished the annular solid is used.

Here, in the polysiloxane shown in the formula (6) and the formula (7), it can set at the rate (6), i.e., the formula, and formula (7) of the silicon atom which the polyoxalkylene group and aromatic ring content organic group to all the siloxane units combined.  $[(I+k)/(m+n+I+k)] \times 100 (\%)$

A denaturation rate will be called.

In order to obtain sufficient foam stability, it is based also on a presentation and the mixture ratio of other ingredients, but 5 to 90% of the above-mentioned denaturation rate is good, and especially 5 to 25% of generally desirable. However, since distribution exists in a denaturation rate, let the numerical value mentioned here be average value. If a denaturation rate is lower than 5%, compatibility with the organic compound which has a carbon-carbon double bond will worsen, foam stability falls, and the cell of foam does not become detailed, but foam breaking arises in the middle of foaming depending on the case, and sufficient expansion ratio may not be obtained. Conversely, if a denaturation rate is higher than 90%, in order for the hydroxilyl group equivalent to become large, to use this compound independently as a hardening agent and to obtain foam, since a large quantity is needed and only foam with low expansion ratio is obtained, it is not desirable.

The rate which the aromatic ring content organic group occupied in the above-mentioned denaturation rate combined, i.e.,  $K_1$ ,  $(I+k)$  can be arbitrarily adjusted in the range which does not produce the adverse effect to the compatibility of the mixture at the time of foam manufacture. As a structure of polyoxalkylene chain, the way with many rates of an oxyethylene unit is preferred, and the rate of an oxyethylene unit over all the oxalkylene units has 50 to 100% of preferred thing at several units. If the rate of an oxalkylene unit is smaller than this, sufficient foam stability will not be obtained.

Although the molecular weight in particular of an oxyalkylene chain is not limited, 100-3000 are preferred at a number average molecular weight, and 200--especially 1000 are preferred. Since sufficient foam stability will not be obtained if a number average molecular weight is smaller than 100, but a large quantity must be used for making it fully harden when manufacturing foam, since the density of a hydroxyl group will fall if conversely larger than 3000, therefore only foam with low expansion ratio is obtained, it is not desirable.

One sort may be independently used for the above-mentioned first - the third hardening agent, and they may use two or more sorts together.

Although it averages in at least one molecule and there should just be a piece about the number of the hydroxyl group in the hardening agent of this invention, more ones are preferred unless compatibility is spoiled. When stiffening the organic compound which has a carbon-carbon double bond by a hydroxylation reaction using the hardening agent of this invention, hardening is slow in the number of this hydroxyl group being less than two pieces, and curing failure is caused in many cases. As for the number of this hydroxyl group, since the hardening agent concerned and an OH radical content compound carry out dehydration condensation and it participates in foaming when applying the hardening agent of this invention to a fizz resin composition, although decided by the target expansion ratio, it is preferred that they are generally three or more pieces. On the other hand, about the maximum of the number concerned, 80 or less are preferred from the ease of acquisition of a compound, the balance of foaming and hardening, etc., and 50 or less are more preferred.

contains the organic compound which contains at least one alkenyl group in (A) intramolecular, (B) organic system hardening agent, and the (C) hydrosilylation catalyst as an essential ingredient. Each ingredient is described below.

(B) As an organic system hardening agent which is the (B) ingredient of ingredient this invention, various kinds of described hardening agents can be used as the first invention, and the thing of the first invention can be applied also to desirable molecular structure.

As a hardening agent which is the (B) ingredient, it is a range which does not affect compatibility with the (A) ingredient and other hardening agents which have a hydroxyl group or a carboxyl group.

(A) If the organic compound which contains at least one carbon–carbon double bond in the molecule which is the (A) ingredient of ingredient, this invention does not have a siloxane bond in a skeleton substantially, there will be no restriction in particular in the structure, and a thing with the various molecular structure of a low molecular weight compound, a polymer, etc. is used.

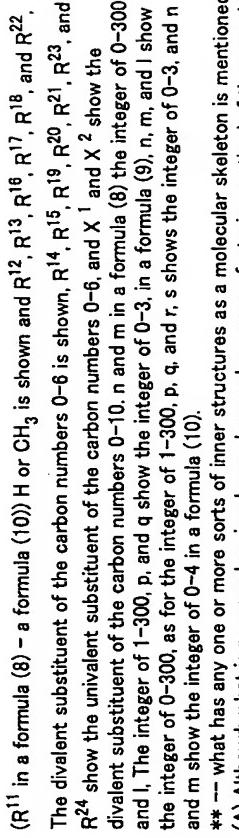
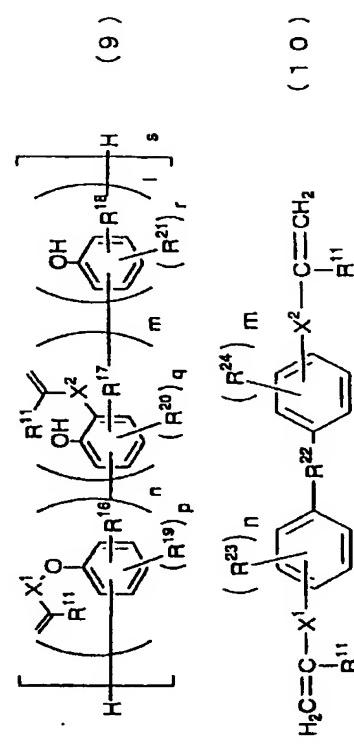
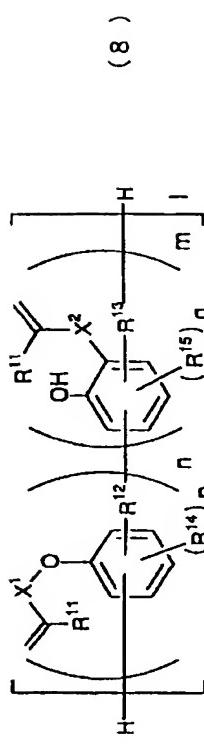
(A) When it divided into the alkene group which has the carbon–carbon double bond which has combined the molecular structure with a skeletal part and its skeleton by the covalent bond in an ingredient and thinks. Although the alkeny group which has a carbon–carbon double bond may exist anywhere in intramolecular, it is preferred to exist in a side chain or an end from a reactant point.

(A) If an ingredient is illustrated concretely, as a low molecular weight compound. Phenol system compounds, such as ether system compounds, such as ester system compounds, such as dially phthalate, and ethylene glycol diaryl ether, 2,6-diarylphenol, and 2,2'-diarylbisphenol A, etc. are mentioned.

It is mentioned as a polymer by what introduced the alkenyl group into the end of various polymers, or the main chain, and as an example of various polymers. A polyoxyethylene, polyoxypropylene, polyoxy tetramethyl, Polyether system polymers, such as a polyoxyethylene polyoxypropylene copolymer. The polyester system polymer obtained by condensation with dibasic acid, such as adipic acid, and glycol, or the ring opening polymerization of lactone. The copolymer of an ethylene-propylene system copolymer, polyisobutylene, isobutylene, isoprene, etc., Polychloroprene, polyisoprene, isoprene, butadiene, acrylonitrile, A copolymer, polybutadiene, butadiene, and styrene etc., A copolymer with acrylonitrile etc., polyisoprene, polybutadiene, The polyolefine system polymer produced by hydrogenating a copolymer with isoprene and acrylonitrile, styrene, etc., The acrylic ester produced

by carrying out the radical polymerization of the monomers, such as ethyl acrylate and butyl acrylate, such as polyacrylic ester, ethyl acrylate, and butyl acrylate, acrylonitrile, methyl methacrylate. An acrylic ester system copolymer with styrene etc., the graft polymer produced by polymerizing a vinyl monomer in said organic polymer, A polysulfide system polymer, Nylon 610 by the condensation polymerization of the nylon 6 by the ring opening polymerization of epsilon-aminocaprolactam, hexamethylenediamine, Nylon 66 by the condensation polymerization of adipic acid and hexamethylenediamine, and sebacic acid, Nylon 11 by the condensation polymerization of epsilon-aminoundecanoic acid. Polyamide system polymers, such as copolyamide which has a two or more-ingredient ingredient among Nylon 12 by the ring opening polymerization of epsilon-amino RAURO lactam, and the above-mentioned nylon. For example, phenol system polymers etc. which were manufactured by carrying out condensation polymerization from bisphenol A and a carbonyl chloride, such as a polycarbonate system polymer, a diallyl phthalate system polymer, novakol resin, and resole resin, are illustrated. Compatibility with the polar high compound of a hydroxyl group content organic system

As a more concrete desirable structure, they are a following general formula (8) – a formula (10).  
hardening agent of the (B) ingredient from the point of harnessing the feature of being good, among compounds with the above-mentioned molecular structure. An ester system compound, an ether system compound, a phenol system compound, a polyester system polymer, an acrylic ester system polymer, an acrylic ester system copolymer, a polyether system polymer, a polycarbonate system polymer, and a phenol system polymer are preferred. Especially the case where it is a compound which contains at least one phenolic group in intramolecular is preferred.



(A) Although what is proposed variously can be used as a manufacturing method of the organic compound which contains at least one alkenyl group in the intramolecular of an ingredient, For example, there is the method of introducing an alkenyl group by making the organic compound which has the active group and alkenyl group which show reactivity to the precursor compound which has functional groups, such as a hydroxyl group, an alkoxide group, a carboxyl group, and an epoxy group, to the above-mentioned functional group react.

As an example of the organic compound which has both the active groups and alkene groups which show reactivity to the above-mentioned functional group, Unsaturated fatty acid of C3-C20, such as acrylic acid, methacrylic acid, vinylacetic acid, acrylic acid chloride, and an acrylic acid star's picture. Acid halide, an acid anhydride, etc. vinyl alcohol and allyl alcohol, a 3-butene-1-oxar, A 4-perten-1-oxar, a 5-hexen-1-oxar, a 6-hepten-1-oxar, A 7-octen-1-oxar, an 8-non-en-1-oxar, a 9-decenes-1-oxar, 2-(allyloxy) ethanol, neopentyl glycol mono-ether, Glycerin diaryl ether, trimethylolpropane diaryl ether, Trimethylolethane diaryl ether netaethoxybutanol triaryl ether

1,2,6-heptanetriol diethyl ether, sorbitan diaryl ether, unsaturation fatty alcohol, such as vinylbenzyl alcohol, allylchloro formate ( $\text{CH}_2=\text{CHCH}_2\text{OCOCl}$ ), C<sub>3</sub> - unsaturation fatty alcohol substitution carbonic acid halide of C<sub>20</sub>, such as allylbromo formate ( $\text{CH}_2=\text{CHCH}_2\text{OCOBr}$ ). An allyl chloride, an allyl star's picture, vinyl(chloromethyl) benzene, Ally(chloromethyl) benzene, allyl(bromomethyl) benzene, Ally(chloromethyl) ether, allyl(chloromethoxy) benzene, 1-buteneyl(chloromethyl) ether, 1-hexenyl(chloromethoxy) benzene, allyloxy (chloromethyl) benzene, an allylosuccinate, allyl phenyl ether etc. are mentioned.

There is also the method of introducing an alkenyl group during a polymerization. For example, when manufacturing the organic polymer of the (A) ingredient by a radical polymerization method, The BINRURU monomer which has a low alkenyl group of radical reactivity in molecules, such as allyl methacrylate and allyl acrylate, An alkenyl group can be introduced into the main chain or end of a polymer by using the radical chain transfer agent which has a low alkenyl group of radical reactivity, such as allyl mercaptan. When producing a rubber-like hardened material using the constituent of this invention, since the effective-network-chain length of a hardened material becomes long, the alkenyl group of the (A) ingredient has a preferred direction which exists in a molecular terminal.

There is the method of using an ester interchange method and introducing an alkenyl group into others. This method is the method of carrying out the ester interchange of the alcohol residue of the ester part of polyester resin or an acrylic resin to alkenyl group content alcohol or an alkenyl group content phenol derivative using a transesterification catalyst. Alkenyl group content alcohol and the alkenyl group content phenol derivative which are used in exchange for alcohol residue. What is necessary is just alcohol or the phenol derivative which has at least one alkenyl groups, such as allyl alcohol, allylglycol, and bisphenol A, and has at least one OH radical. Even if it uses a catalyst, it is not necessary to carry out but, and when using it, the catalyst of acid, a titanium system, an aluminum system, or a tin system is preferred. Specifically, diaryl carbonate, such as bisphenol A, bis(methyl)acrylic ester, etc. are mentioned.

Although the compound which contains one or more phenolic hydroxyl groups in intramolecular as mentioned above is preferred as a (A) ingredient of this invention, as a method of manufacturing this compound, For example, phenol, cresol, xylene, resorcinol, catechol, The novolac and/or resol type phenol using a BIROGA roll etc., To bisphenol system compounds, such as bisphenol A, the bisphenol F, the bisphenol S, and tetrabromobisphenol A. The method of introducing an alkenyl group is mentioned by making the organic compound which has both an active group which shows reactivity to a phenolic hydroxyl group, and an alkenyl group react. As a concrete reaction, phenols and allyl chlorides, such as O,O'-diaryl bisphenol A and 2,2'- diarylbisphenol A, A method to which an allyl bromide etc. are made to react under base catalyst existence, and a method to which phenols, such as bisphenol A, are made to react under allyl glycidyl ether, glycidyl methacrylate, etc. and an epoxidation catalyst. The method to which an isocyanate, allyl alcohol, or allylamines, such as 4,4'-methylenebis (phenylisocyanate) and tolylene 2,6-diisocyanate, are made to react under urethane-ized catalyst existence is illustrated. The principal chain skeleton which has functional groups, such as OH radical, an alkoxide group, a carboxyl group, and an epoxy group, in an end, a main chain, or a side chain is compounded beforehand if needed, and there is also the method of introducing an alkenyl group by the method illustrated by the above-mentioned method.

There is the method of using for all elsewhere the compound which has an alkenyl group in part, and compounding a phenol resin skeleton. This is a method to which the aromatic compounds which have a double bond, and phenols are made to react by formaldehyde or diisocyanate for example, and, specifically, is the method of carrying out the polycondensation of allylphenol and other phenols by formaldehyde etc. under acid or base existence. The allyl ether system compound etc. which are produced by allyl alcohol, allylglycol, etc. carrying out Michael addition can be used to bis(methyl)acrylic ester.

There is no restriction in particular in the bond form of above alkenyl groups and organic compounds, and what this alkenyl group else [ in the case of coupling directly by carbon-carbon bonding ] has combined with the organic compound via ether, ester, carbonate, amide, a urethane bond, etc. is illustrated.

(A) About the molecular weight of an ingredient, 100~50000 are preferred from points, such as the characteristic of a hardened material, and compatibility with the (B) ingredient, and 100~especially 20000 are preferred.

(A) As for the number of the carbon-carbon double bonds of the organic compound of an ingredient, it is preferred to exceed 1.0 piece by the average per molecule, and it is preferred that they are especially two or more pieces [ five or less ]. (A) When the number of the carbon-carbon double bonds of 1 intramolecular of an ingredient is one or less, it is because it does not

become the structure of cross linkage only by becoming graft structure even if it reacts to the (B) ingredient.

As for the ratio of the above-mentioned (B) ingredient and the (A) ingredient, 0.2~50 are preferred at the mole ratio to the alkenyl group of a hydroxyl group, and 0.4~25 are more preferred. Only a hardened material with insufficient hardening and intensity small when a mole ratio becomes smaller than 0.2, and the constituent of this invention is hardened with greatness is obtained. When a mole ratio becomes larger than 50, since a hydroxyl group [ activity / in a hardened material ] remains so much, a crack and a void occur, it is uniform and after hardening has the tendency for a hardened material with intensity not to be obtained.

(C) About the hydrosilylation catalyst which is the (C) ingredient of ingredient, this invention, the arbitrary things which have restriction [ be nothing ] can be used especially. The catalyst, same with having specifically described the hydroxyl group content organic system hardening agent which is the 1st invention can be used. These catalysts may be used alone and may be used together two or more sorts. Chloroplatinic acid, a platinum-olefin complex, a platinum-vinyl siloxane complex, etc. are preferred from a point of catalytic activity. Although there is no restriction in particular as a catalyst amount, it is good to use in the range of a  $10^{-1}$  ~  $10^{-8}$  mol to 1 mol of alkenyl groups in the (A) ingredient. It is good to use in the range of a  $10^{-3}$  ~  $10^{-6}$  mol preferably.

When preparing other ingredient hardened materials, to everything but three ingredients, (A), (B), and (C) According to the purpose of use, a solvent, an adhesive improving agent, a physical-properties regulator, a preservation stability improving agent. Various additive agents, such as a plasticizer, a bulking agent, an antiaging agent, an ultraviolet ray absorbant, a metal deactivator, anti-ozonant, light stabilizer, amine system radical chain inhibitor, the Lynn system peroxide decomposition agent, lubricant, paints, a foaming agent, and fire retardant, can be added suitably.

As an example of the above-mentioned bulking agent, for example Glass fiber, carbon fiber, mica, Graphite, diatomite, clay, fume silica, sedimentation nature silica, A silicic acid anhydride, alumina, carbon black, calcium carbonate, clay, Talc, titanium oxide, magnesium carbonate, barium sulfate, quartz, aluminum impalpable powder, the Flint powder, zinc dust, an inorganic balloon, GOMIGURA nu, wood flour, phenol resin, melamine resin, vinyl chloride resin, etc. are mentioned.

As the above-mentioned antiaging agent, the antiaging agent generally used, for example, citrate and phosphoric acid, a sulfur-systems antiaging agent, etc. are used.

As the above-mentioned sulfur-systems antiaging agent, mercaptans, the salts of mercaptan, Sulfide carboxylate and the sulfides containing hindered phenol system sulfides. Polysulfide, dithiocarboxylic acid salts, thiourea, thio phosphate, a sulfonyl compound, thioaldehydes, thioketones, mercaptal, mercaptol, monothio acid, polythio acid, thioamides, and sulfoxides are mentioned.

As the above-mentioned radical inhibitor, for example A 2,2'-methylene-screw (4-methyl-6-t-butylphenol), Phenol system radical inhibitor, such as tetraakis (methoxy-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate) methane, Amine system radical inhibitor, such as phenyl-beta-naphthylamine, alpha-naphthylamine, the NN'-second butyl-p-phenylene diamine, phenothiazin, and N,N'-diphenyl-p-phenylene diamine, etc. are mentioned.

As the above-mentioned ultraviolet ray absorbent, 2 (2'-hydroxy-3',5'-di-t-butylphenyl) benzotriazol, bis(2,2,6,6-tetramethyl 4-piperidine)sebacate, etc. are mentioned, for example.

As the above-mentioned adhesive improving agent, the compound of silane coupling agents, such as adhesives generally used, an amino silane compound, an epoxysilane compound, and others can be used. As an example of such an adhesive improving agent, phenol resin, an epoxy resin, gamma-aminopropyl trimethoxysilane, N-(beta-aminooethyl) aminopropyl methyl dimethoxysilane, Coumarone-indene resin, rosin ester resin, terpene phenol resin, a alpha-methylstyrene vinyltoluene copolymer, polyethylmethylstyrene, alkyl titanate, aromatic polysocyanate, etc. can be mentioned.

As the above-mentioned fire retardant, tetrabromobisphenol A, tetrabromobisphenol A epoxy,

Halogen system agents, such as decabromo diphenyloxide, triethyl phosphate, Tricresyl phosphate, tris (chloroethyl) phosphate, Inorganic flame retardants, such as phosphorus series flame retardants, such as tris (chloropropyl) phosphate, tris (dichloropropyl) phosphate, polyphosphoric acid ammonium, and red phosphorus, aluminium hydroxide, magnesium hydroxide, antimonous oxide, and antimony pentoxide, etc. are raised. One sort may be alone used for these fire retardant, or it may use two or more sorts together. The manufacture above (A) and the (B) ingredient of a hardened material, and the uniform hardened material which was excellent in depths hardenability without being accompanied by phenomena, such as foaming, when mixing and softening other addition ingredients the (C) ingredient and if needed further preferably are obtained.

The description of a hardened material can be manufactured from a rubber-like thing to a resin-like thing, although it is dependent on a principal chain skeleton, a molecular weight, etc. of the polymer of (A) and the (B) ingredient, to be used. Although there is no restriction in particular about curing conditions, it is good to harden at 30–150 \*\* preferably at 0–200 \*\* generally for 10 seconds – 4 hours. At the elevated temperature in 80–150 \*\*, what is hardened in a short time of 10 seconds – about 1 hour is obtained especially.

Although there is no limitation in particular about the combination method of a constituent, after preparing two or more sorts of constituents which use each (A) and (B) ingredient of a hardenability constituent as a substantial ingredient from the field of workability, it is desirable by mixing them to make it harden. What is necessary is for there to be no restriction in particular also in the addition method of the (C) ingredient which is a catalyst, and just to choose an easy method on work, and even if it mixes and uses for one of the (A) ingredient and the (B) ingredients, simultaneously with mixing of the (A) ingredient and the (B) ingredient, it may add after a mixed end.

As the concrete method of hardened material manufacture, if needed, just before using the hardenability constituent of this invention, a catalyst, and 2 that mixed the additive agent a priori in a suitable combination liquid, or the separate mixture of the number beyond it, it mixes, and extrusion or the method of making it pour in is still more desirable. Especially as a mixing method, although not limited, methods usually used with urethane resin, an epoxy resin, and phenol resin, such as hand mixing, an electric mixer, a static mixer, and collision mixing, can be used.

3. Fizz resin composition The fizz resin composition concerning the third invention contains further the compound which has the (D) foaming agent and/or an OH radical in the hardenability constituent of the second invention as an essential ingredient. It hardens by performing added type crosslinking reaction by the hydrosilylation reaction for which the (A) ingredient and the (B) ingredient generate a Si–C combination excellent in weatherability in the fizz resin composition of this invention. A foaming agent evaporates or decomposes with the reaction fever of the aforementioned (A) ingredient and the (B) ingredient simultaneously with this, or it foams by the (B) ingredient and the (D) ingredient reacting and generating hydrogen gas, and foam is formed.

That is, in the fizz resin composition of this invention, that compressive strength, paintwork, an adhesive property, stain resistance, whose dust sticking nature, etc. improved is obtained compared with silicone foam at the time indicated by said advanced technology by using the organic compound which does not include siloxane units in a molecular skeleton as a (A) ingredient.

what has broad physical properties, such as half rigidity and elasticity, is obtained from hard by boiling various (B) ingredients and changing them. Expansion ratio can obtain foam with a high rate of a closed cell highly by using especially the compound which has a specific structure as a (B) ingredient. As an organic system hardening agent which is the (B) ingredient of this invention, various kinds of hardening agents explained by the first invention can be used, and what was described by the first and the second invention also about concomitant use with desirable molecular structure and other hardening agents can be applied.

There is no restriction in particular as an organic compound which contains at least one carbon–carbon double bond in the molecule which is the (A) ingredient of this invention, and a thing with the various molecular structure of a low molecular weight compound as the second invention explained, a polymer, etc. can be used.

(A) As for the skeleton of an ingredient, it is preferred that compatibility with the (B) ingredient is what harnesses the feature of being good. As for siloxane units (Si–O–Si) like polysiloxane organicity block copolymer or a polysiloxane organicity graft copolymer, what is a skeleton which does not contain but contains any one or more sorts in carbon, oxygen, hydrogen, nitrogen, sulfur, and halogen as a composing element is preferred. For example, they are skeletons, such as a polyether system, a polyester system, a polycarbonate system, a saturated hydروcarbon system, a polyacrylic ester system, a polyamide system, and a phenoformaldehyde system (phenol resin system). As a monomer skeleton, a phenol system, bisphenol systems, or these mixtures are mentioned for example.

Among these, a polyether system polymer skeleton is suitably used, in order to obtain elastic foam. As the example, a polyoxyethylene, polyoxypropylene, polyoxytetramethylen, a polyoxyethylen polyoxypropylene copolymer, etc. are mentioned. In order that other polymer skeletons with high Tg may also obtain foam on the other hand compared with a polysiloxane

skeleton, it is used suitably. Uniform mixing with other ingredients is possible for the organic compound of the (A) ingredient, and it is preferred that it is liquid at the temperature of 100 \*\* or less so that foam may be obtained by a spray, pouring, etc. Although a line or the letter of branching may be sufficient as the structure and a molecular weight in particular is not limited, about 100 to 100,000 arbitrary things can use it conveniently, and if it is an organic polymer, especially the thing of 500–20,000 is preferred. There is a tendency which the feature by use of organic polymers, such as grant of flexibility [molecular weight / 500 / less than ], cannot reveal easily, and the effect of bridge construction by the reaction of an alkanyl group and a hydroxyl group cannot reveal easily if a molecular weight exceeds 100,000.

(D) Describe the compound which has the foaming agent and OH radical of an ingredient, next the (D) ingredient. About a foaming agent and the compound which has an OH radical, it may use independently, respectively or may use together. It is possible to choose from what restriction in particular does not have in the kind of foaming agent, for example, is usually used for organic foam, such as polyurethane, phenol polystyrene, and polyolefine, and to use. In order to manufacture stable foam, the method of adding to a constituent beforehand by using a volatile compound as a foaming agent, and making it foam with generation of heat or decompression is preferred.

When a foaming agent is a volatile compound as for the boiling point, 100 \*\* or less is preferred, its 80 \*\* or less is more preferred, and especially its 50 \*\* or less is preferred. Considering the device to be used, the ease of handling, etc., a -30 \*\* to about 35 \*\* thing has the preferred boiling point.

As for the solubility to the (A) ingredient of a foaming agent, in 23 \*\*, five or more weight sections are preferred to (A) ingredient 100 weight section, its ten or more weight sections are more preferred, and its 15 or more weight sections are still more preferred. If there is less solubility than five weight sections, since the cell of foam will be ruined, it is not desirable, and the foam of desired high magnification is hard to be obtained.

The solubility to the (A) ingredient of a foaming agent is called for, for example by the following method. If the boiling point of a foaming agent is not less than 23 \*\*, with a described method when measurement is difficult, After carrying out weighing of the (A) ingredient and the foaming agent to the resisting pressure container of volume known, from the volume and the pressure of a cavity part of a resisting pressure container, the quantity of an insoluble foaming agent can be calculated and it can ask for solubility based on this.

Although the kind in particular of foaming agent is not limited, it is preferred independent, to use

two or more sorts together, and to use the compound chosen from organic compounds, such as hydrocarbon, a ketone system compound, chlorofluorocarbon, and ether, carbon dioxide, nitrogen, air, etc. from the field of workability and safety.

As hydrocarbon, methane, propane, n-butane, isobutane, N-pentane, isopentane, a neopentane, n-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, cyclopentane, a cyclobutane, cyclopentene, cyclohexane, etc. are mentioned. Propane, n-butane, isobutane, n-pentane, and cyclopentane are [ among these ] preferred from the ease of handling, etc.

As an example of a ketone system compound, acetone, methyl isopropyl ketone, etc. are mentioned.

As chlorofluorocarbon, trichlorofluoromethane (R1), dichlorodifluoromethane (R12), Chlorotrifluoromethane (R13), bromotrifluoromethane (R13B1), Tetrafluoromethane (R14), dichlorofluoromethane (R21). Chlorodifluoromethane (R22), trifluoromethane (R23).

Difluoromethane (R32), fluoromethane (R41), tetrachlorodifluoroethane (R112),

Trichlorofluoroethane (R113), the dichlorotetrafluoroethane (R114), Dibromo tetrafluoro ethane (R114 B-2), chlоро pentfluoro ethane (R115), Hexafluoroethane (R116), chlorotrifluoroethane (R123), Tetrafluoro ethane (R141a), dichlorofluoroethane (R141b), Chlоро difluoroethane (R142b), difluoroethane (R152a), Octafluoropropane (R218), dichloropentafluoropropane (R225), hexafluoropropane (R236a), pentafluoropropane (R245fa), octafluorocyclobutane (RCB18), Hexafluoro butane (R235fa), pentafluorobutane (R4310me), etc. are mentioned.

When an environmental problem etc. are taken into consideration, hydrochlorofluorocarbon (HCFC) and what is called a chlorofluorocarbon alternative are preferred, and also it is more preferred than chlorofluorocarbon (CFC) especially to use hydrofluorocarbon (HFC). That is, tetrafluoro ethane, difluoroethane, octafluoropropane, hexafluoropropane, pentafluoropropane, octafluorocyclobutane, hexafluoro butane, and especially pentafluorobutane are excellent. As ether, wood ether, diethyl ether, ethylmethyl ether, tert-butylmethyl ether, tert-butylethyl ether, 1,1-dimethyl propylmethyl ether, methyl pentanofluoroethyl ether, Dipropyl ether, diisopropyl ether, butylmethyl ether, Butylketyl ether, tert-butylmethyl ether, tert-butylethyl ether, 1,1-dimethyl (trifluoromethyl) tetrafluoro ethyl ether, etc. are mentioned.

As a foaming agent suitably used also in the above, although based on the structure of the (A) ingredient etc., The carbon number 2 whose solubility at 23 \*\* [ as opposed to / hydrocarbon and chlorofluorocarbon are mentioned and / (A) ingredient 100 weight section ] is five or more weight sections also in these, or 3 hydrofluorocarbon (HFC). Any one or more sorts chosen from among the hydrochlorofluorocarbon (HCFC) of the carbon numbers 1-3, hydrocarbon of the carbon numbers 3-6, the carbon number 3 - 50 ketone system compounds, and the ether of the carbon numbers 2-6 are used especially suitably. From points, such as an environmental problem, hydrocarbon, hydrochlorofluorocarbon (HCFC), and hydrofluorocarbon (HFC) are preferred.

As other foaming methods, for example  $\text{NaHCO}_3 \cdot 2\text{CO}_3(\text{NH}_4)$ ,  $\text{NH}_4\text{HCO}_3 \cdot \text{NH}_2\text{NO}_2 \cdot \text{Ca}(\text{N}_3)_2$ , Inorganic system foaming agents, such as  $\text{NaBH}_4$ , AZOJ1 carvone amide, azobisisobutyronitrile, It is also possible to use together \*\*\*, such as generating of the carbon dioxide by the reaction of organic system foaming agents, such as bariumazo dicarboxylate, dinitrosopentamethylene tetramine, and paratoluene sulfonyl hydrazin, an isocyanate, and active hydrogen group containing compounds and mechanical stirring.

Next, the compound which has an OH radical is described.

Although the kind in particular of compound which has an OH radical used by this invention is not limited, not the OH radical content (poly) siloxane mostly used by conventional silicone foam but compatibility with other ingredients is good, and what does not include a siloxane bond in a molecular skeleton is preferred. It is preferred to specifically use both an organic compound, and both [ either or ] which the OH radical couples directly with the carbon atom, and the effect which uses the organic compound which has a carbon-carbon double bond by this becomes more remarkable. The compounds which the OH radical couples directly with the carbon atom

are alcohols and carboxylic acid.

As alcohols, methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, tert-butanol, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Ethylene glycol monophenyl ether, Univalent alcohol, such as ethylene glycol monoallyl ether and glycerin diaryl ether, Ethylene glycol, propylene glycol, a 1,4-butylene glyco, A 1,3-butylene glyco, A 2,3-butylene glycol, a diethylene glycol, neopentyl glycol, 1,6-hexamethylene glycol, 1,9 - a crucian carp — methylene glycol, glycerin, and trimethylpropane, polyether polyol (sorbitol), such as polypropylene glycol, polyethylene glycols and these copolymers, and glycerin monoallyl ether, a polypropylene glycol, polyethylene glycols and these copolymers, and sucrose, tetraethylenglycol, etc. What contains three or more OH radicals in the monad which used such as horse mackerel peat system polyol, polycaprolactone system polyol, and polycarbonate system polyol. Phenol system polyols, such as epoxy denaturation polyol, polyether ester polyol, and benzylc ether type phenol polyol, Fluoride polyols, such as Lumiflon (made by Asahi Glass Co., Ltd.), polybutadiene polyol, Hydrogenation polybutadiene polyol, castor oil system polyol, containing halogen fire retardancy polyol, The Lynn content fire retardancy polyol, phanol, cresol, a xyleneol, Resorcinol, catechol, pyrogallol, bisphenol A, the bisphenol B. The compound which has phenolic hydroxyl groups, such as the bisphenol S and phenol resin, 2-hydroxyethyl (meta) acrylate, 2-hydroxpropy (meta) acrylate, ARONIKUSU 5700 made from 2-hydroxyethyl vinyl ether, N-methylol(metha)acrylamide, and Tohosei Chemical industry, 4-hydroxystyrene, HE-10 by Nippon Shokubai Kagaku Kogyo Co., Ltd., HE-20, HP-10 and HP-20 (acrylic acid ester oligomer to which all have an OH radical at the end), The BUREMMA PP series by Nippon Oil & Fats Co., Ltd. (polypropylene-glycol methacrylate), BUREMMA PE series (polyethylene glycol monomethacrylate), BUREMMA PEP series (polyethylene-glycol polypropylene-glycol methacrylate), BUREMMA AP-400 (polypropylene-glycol monacrylate), BUREMMA AE-350 (polyethylene-glycol monacrylate), BUREMMA NKH-5050 (polypropylene-glycol poly trimethylene monooacrylate) and BUREMMA GLM (Glycerol mono- methacrylate), OH radical content vinyl system monomers, such as epsilon-caprolactone denaturation hydroxalkyl vinyl system monomer obtained by the reaction of an OH radical content vinyl system compound and epsilon-caprolactone (these can be used also as a combination substance of the (A) ingredient and the (D) ingredient). The acrylic resin which has an OH radical which can be obtained by copolymerization with said OH radical content vinyl system monomer, acrylic acid, methacrylic acid, those derivatives, etc., other alkyl resin, The resin which has OH radicals, such as an epoxy resin, is mentioned.

Also in these OH radical content compounds, by the evaporation, the evaporation, etc. by generation of heat of hardening reaction time, coalescence of air bubbles. Since it does not have adverse effects, such as hypertrophy and foam breaking, with a carbon numbers of three or more alcohol has it, and specifically, [ desirable ] n-propanol, iso-propanol, n-butanol, iso-butanol, tert-butanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, etc. are preferred. Even if the ease of a reaction with a hydroxyl group and dehydration condensation furthermore advance, bridge construction does not take place. And especially the 1st class alcohol, such as n-propanol from the field of the bad smell in the case of handling, n-butanol, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, and ethylene glycol monophenyl ether, is preferred. On the other hand as carboxylic acid, acetic acid, propionic acid, n-butanoinic acid, isobutyric acid, n-valeric acid, hexanoic acid, 2-ethylhexanoic acid, malonic acid, adipic acid, meso-1,2,3,4-tetracarboxylic acid, benzoic acid, phthalic acid, isophthalic acid, terephthalic acid, etc. are mentioned. Also in this, carboxylic acid univalent from bridge construction not taking place, even if the ease of a reaction with a hydroxyl group and dehydration condensation advance is preferred, and especially 2-ethylhexanoic acid is still more preferred from the field of the bad smell at the time of handling.

In order that the volume of the OH radical content compound which will be added if a hydroxy

equivalent becomes large may become large and expansion ratio may not increase, the compound of 1 - 33 mmol/g has a preferred hydroxyl equivalent, and the thing of 2.5 - 25 mmol/g is more preferred from a reactant point.

It is also possible to use together two or more kinds of OH compounds for adjustment of foaming speed. As an example used together, the combination of the 1st class alcohol, such as n-propanol, the 2nd class alcohol, such as iso-propanol, carboxylic acid and the 1st class alcohol or carboxylic acid, and water is preferred. Furthermore, for adjustment of cure time, ethylene glycol, propylene glycol. The multivalent OH compound and ethylene glycol monoallyl ether more than divalent [ of 1,4-butanediol, glycerin, etc. ]. Glycerin monoallyl ether, glycerin diethyl ether, pentaerythritol diaryl ether. The compound having both the carbon-carbon double bonds and OH radicals which can be hydroxylated to intramolecules, such as pentaerythritol triaryl ether and undecylenic acid, can also be used.

Since the structure of cross linkage is made while generating hydrogen gas at the reaction of the (B) ingredient and the (D) ingredient when the (D) ingredient which has two or more OH radicals is used for 1 intramolecular, it is possible to use a small quantity auxiliary for adjustment of cure time, but Using so much is not desirable in order to harden before performing sufficient foaming. The compound which has a carbon-carbon double bond and an OH radical can also be used for 1 intramolecular as a combination substance of the (A) ingredient and the (D) ingredient. The blending ratio, the above (A), (B), and (D), of three ingredients, Although it is suitably chosen by the structure of each ingredient, the expansion ratio made into the purpose, and the physical properties made into the purpose and limitation in particular is not carried out, the number  $x$  of mols of the hydroxyl group of the (B) ingredient (A) It is preferred that ratios with the sum of the number  $y$  of mols of the carbon-carbon double bond of an ingredient and the number  $z$  of mols of the OH radical of the (D) ingredient are  $x+y+z=30:1 - 1:30$ . It is  $x+y+z=10:1 - 1:10$  still more preferably. If the mole ratio of a hydroxyl group exceeds  $x+y+z=30:1$ , crosslinking density will become low, sufficient mechanical strength is not obtained, and sufficient foaming and hardening do not take place with it being less than  $[x+y+z=1:30]$ .

According to the skeleton of the expansion ratio which limitation in particular does not have in the ratio of the number  $y$  of mols of the carbon-carbon double bond of the (A) ingredient, and the number  $z$  of mols of the OH radical of the (D) ingredient, and is made into the purpose, the physical properties made into the purpose, and the (B) ingredient, the kind of (D) ingredient, etc., although it can select suitably. Generally  $y+z=100:1 - 1:100$  are preferred and  $y+z=10:1 - 1:20$  are more preferred.

In this invention, the catalyst for dehydratation condensation with the aforementioned (B) ingredient and the (D) ingredient and the addition reaction (hydroxylolation reaction) of the (A) hydroxylolation catalyst and co-catalyst, the amount used, etc. also to this invention.

What was described about the first and the second invention can apply the kind of a antiaging agent, radical inhibitor, an ultraviolet ray absorbent, an adhesive improving agent. Foam stabilizers, such as fire retardant, a poly dimethylsiloxane polyalkylene oxide system surface-active agent, or organic surfactants (polyethylene glycol alkylphenyl ether etc.). Acid or a basic compound (it is an additive agent for reaction adjustment with a hydroxyl group and an OH radical, and) A condensation reaction is inhibited from acid and it accelerates by a base. A preservation stable improving agent, anti-ozonant. In the range which does not spoil the purpose and effect of this invention, light stabilizer, a thickener, a plasticizer, a coupling agent, an antioxidant, a thermostabilizer, an electro-conductivity applying agent, a spray for preventing static electricity, a radiation interception agent, a nucleating additive, the Lynn system peroxide decomposition agent, lubricant, paints, a metal deactivator, a physical-properties regulator, etc. can be added.

The example of the above-mentioned bulking agent, an antiaging agent, radical inhibitor, an ultraviolet ray absorbent, an adhesive improving agent, and fire retardant is as the second invention having explained. Foam is manufactured by mixing and carrying out foam curing of a catalyst and the other

additive agents to the fizz resin composition of this invention in which foam carried out the manufacture above if needed.

The temperature which carries out foam curing is preferred, and when it considers application to foaming in place, it is more preferred. [ of the thing near ordinary temperature ] [ of 100 °C or less ] In the elevated temperature over 100 °C, it is hard to balance foaming by the hydrogen gas for addition with (A) ingredient and (B) ingredient type bridge construction (hardening) reaction velocity to become large too much, and emitted at the reaction of the (B) ingredient and the (D) ingredient.

Manufacture of the foam concerning this invention The fizz resin composition and catalyst of this invention, 2 liquid or the number beyond it of separate mixtures furthermore mixed a priori if needed combining an additive agent suitably can be mixed just before use, and it can carry out by the method which apply to a base material surface directly and it is made to carry out foaming in place, and the method of mixing and carrying out foaming in place, just before using the same mixture. As a mixing method, methods, such as hand mixing, an electric mixer, a static mixer, and collision mixing, can be used. When carrying out especially foaming in place, it is preferred to use a static mixer or collision mixing.

Although the following is mentioned as how to combine the fizz resin composition and catalyst of this invention in the case of using an additive agent as 2, a priori mixed liquid or number beyond it of separate mixtures if needed further. Before mixing all the ingredients, what is necessary is just the combination about which generating or hardening of hydrogen do not advance, and it is not limited to these. Namely, the mixture of the (2) and (A) ingredient used as 2 liquid of a part of (1) and (B) ingredient and the mixture of the (A) ingredient, and a mixture with a part of (B) ingredient, the (D) ingredient, and the (C) ingredient, the (D) ingredient, and the (C) ingredient, (B) it is considered as 2 liquid only with an ingredient, or is considered as 2 liquid of the mixture of the (3) and (A) ingredient, the (D) ingredient, and the (C) ingredient, and the mixture of the (B) ingredient and the (D) ingredient — it is \*\*.

The forming process in particular of foam is not restricted, either, but various foam molding methods used for manufacture of polyurethane foam, phenolic foam, silicone foam, etc., such as the extrusion foaming method, a continuation foaming method, a cast molding method, a discontinuous forming process, or a foaming-in-place execution method, can use suitably. It fabricates with painting tools, such as the slab foaming method made to foam freely on the paper or the plastic film which it lets out continuously on a band conveyor as the above-mentioned continuation foaming method, paper, plywood, a metal plate, and the double conveyor method etc. to laminate are used. A cast molding method is the method of completing the mold goods which carried out regurgitation foaming into the mold of desired shape, carried out cure hardening, and accompanied the inner surface shape of the mold. A discontinuous forming process is used for shaping of a sandwich panel etc.

As the site operation method, there are a 1 liquid type simple spray method, a 2 liquid type spray method, a 2 liquid mold injection method, the 2 liquid type applying method, etc., and it is mainly used for a construction heat insulation use. Although there is no restriction in particular in the expansion ratio per unit volume with which the foam in this invention was expressed as  $(\text{volume of foam}) / (\text{volume of the opening in the volume-foam of foam})$ , it is preferred to have [ which becomes remarkable / the useful feature by being foam ] especially expansion ratio of 4 times or more more than twice. As described above, the fizz resin composition of this invention has the effect that foaming in place is possible since it foams under low-temperature heating comparatively, and it is possible to lower the price per unit volume ordinary temperature or by being low toxicity and raising expansion ratio excluding an isocyanate.

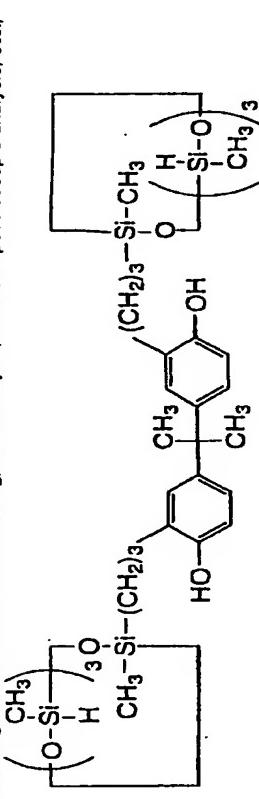
According to the manufacturing method of this invention using this fizz resin composition, the foam which has the outstanding feature that weatherability, paintwork, and an adhesive property are good and no generating of gas harmful at the time of combustion is obtained. And by selection of the presentation (a skeleton and the molecular weight between the points constructing a bridge) of the (A) ingredient, the rate of a compounding ratio of each ingredient, etc., it can manufacture from rigid foam to soft foam, and expansion ratio can also be set up

from low magnification to high magnification. The cellular structure becomes possible [ manufacturing detailed and uniform foam ] chemical blowing, that the reaction velocity of bridge construction can be controlled, and by using the compound which has a specific structure in the (B) ingredient.

[Example]

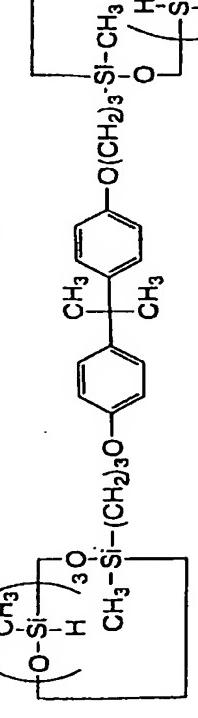
Next, an example explains this invention still more concretely. However, this invention is not limited to the following examples.

1504g of 1,3,5,7-tetramethyl cyclotetrasiloxane (product [ made from Shin-etsu Chemicals ] KF9302) and 500 ml of toluene were put into the 4 poem round bottom flask of 3L provided with synthetic example 1 thermometer, the agitating equipment child, the tap funnel, and the capacitor under a nitrogen atmosphere. Xylene solution 47.2ml (a platinum atom is used and it is  $6.2 \times 10^{-6}$  mol) of the bottom of stirring and a platinum-vinyl siloxane complex was dissolved in 20 ml of toluene at the room temperature, and it added. What warmed at 70 \*\* and dissolved the 2,2'-diarylbisphenol A 192g in 200 ml of toluene under stirring was added from the tap funnel over 30 minutes. The tap funnel was washed with 30 ml of toluene after the end of addition. After stirring the obtained solution at 70 \*\* for 2 hours, 16.7 mg of benzothiazole was added. Toluene and unreacted tetramethyl cyclotetrasiloxane were distilled off under decompression, and the consistency brown [ 470 g of ] fluid was obtained. It is a formula by analysis of the nuclear magnetic resonance of this thing, mass analysis, infrared spectroscopic analysis, etc.:



It came out and was identified the compound expressed.

500g of 1,3,5,7-tetramethyl cyclotetrasiloxane and 150 ml of toluene were put into the 4-poem round bottom flask of 2L provided with synthetic example 2 thermometer, the agitating equipment child, the tap funnel, and the capacitor under a nitrogen atmosphere. Xylene solution 15.6ml of the bottom of stirring and a platinum-vinyl siloxane complex was dissolved in 20 ml of bisphenol A diaryl ether in 60 ml of toluene under stirring was added from the tap funnel over 30 minutes. The tap funnel was washed with 20 ml of toluene after the end of addition. After stirring the obtained solution at 70 \*\* for 2 hours, 4.7 mg of benzothiazole was added. Toluene and unreacted tetramethyl cyclotetrasiloxane were distilled off under decompression, and the 165-g a little consistency fluid of thin yellow was obtained. It is a formula by analysis of this thing nuclear magnetic resonance, mass analysis, infrared spectroscopic analysis, etc.:



It came out and was identified the compound expressed.

The condenser tube and thermometer which attached the method tap of three to a rabbie, a dropping funnel, and the upper part were set to the 4 mouth flask of 31 l. of synthetic examples. Xylene solution 241ml of 1, 3, 5, 120 g of 7-tetramethyl cyclotetrasiloxane, and a platinum-vinyl siloxane complex and 120 ml of toluene were put into this flask. Mixed liquor was heated at 80 \*\* and O-allylphenol 67.0g (0.50 mol) was dropped over 20 minutes from the dropping funnel. It agitated as it is at 80 \*\* for 2 hours.

It checked that the peak of the vinyl group had disappeared the reaction mixture by measurement of nuclear magnetic resonance, and after cooling, the activated carbon 10g was added and it agitated at the room temperature for 1 hour. The methyl hydrogen cyclosiloxane which denaturalized by 3-(2-hydroxyphanyl) propyl group was obtained a little as viscous liquid by filtering a mixture and condensing filtrate. It was 8.1 mmol/g when the SiH value of this polysiloxane was measured.

The condenser tube, thermometer which connected the method tap of three to synthetic example 4 dropping funnel and the upper part, In the 4 Thu mouth flask which connected the mechanical stirrer, 60.1 g of 1,3,5,7-tetramethyl cyclotetrasiloxane was put in, and it heated at 40 \*\* passing oxygen / nitrogen mixed gas (1% of oxygen content) from the method tap of three. 6.5 mg of Pt-vinyl siloxanes (3% xylene solution) were put in, the O,O'-diarylbisphenol A 30.8g was dropped from the dropping funnel, and the end trickled after that 8.1 g of polyethylene oxide polymers (number average molecular weight 400) replaced by the allyl group and the methyl group. After agitating at 40 degrees then for 1 hour and completing a reaction, benzothiazole was added as stabilizer. A little \*\*\*\* transparent liquid was obtained by heating under decompression of a reaction mixture and distilling off volatile matter content.

The condenser tube and thermometer which attached the three-way cock to a rabbie, a dropping funnel, and the upper part were set to the 4 mouth flask of 51 l. of synthetic examples. Xylene solution 241ml of 120 g of 1,3,5,7-tetramethyl cyclotetrasiloxane and a platinum-vinyl siloxane complex was put into this flask. Mixed liquor was heated at 40 \*\* and 11.8 g (0.10 mol) of alpha-methylstyrene was dropped over 5 minutes from the dropping funnel. It checks that the peak of a vinyl group has disappeared the reaction mixture by  $^1\text{H-NMR}$  after 30-minute churning. Next, another [ a methyl group and ] end trickled 70 g (0.20 mol of allyl groups) of ethylene oxide polymers (number average molecular weight 350) which denaturalized, respectively over 10 minutes by the allyl group, and the piece end agitated as it is at 80 \*\* after the end for 2 hours.

It checked that the peak of the vinyl group had disappeared the reaction mixture by  $^1\text{H-NMR}$ , and after cooling, the activated carbon 10g was added and it agitated at the room temperature for 1 hour. The mixture was filtered and the cyclotetrasiloxane which denaturalized by the phenethyl group and the polyoxyalkylene group was obtained as viscous liquid. It was 8.3 mmol/g when the SiH value of this polysiloxane was measured.

According to the example 4 of synthetic example 6 composition, xylene solution 241ml of 120 g of poly(organohydrogen siloxanoxane (product [ made from Shin-etsu Chemicals ] KF-930), 120 ml of toluene, and a platinum-vinyl siloxane complex was put in instead of 1,3,5,7-tetramethyl cyclotetrasiloxane. Mixed liquor was heated at 80 \*\*, and like the synthetic example 5, 11.8 g of alpha-methylstyrene and the ethylene oxide polymer 70g were dropped over 10 minutes from the dropping funnel, and it agitated as it is at 80 \*\* after the end for 2 hours.

It checked that the peak of the vinyl group had disappeared the reaction mixture by  $^1\text{H-NMR}$ , and after cooling, the activated carbon 10g was added and it agitated at the room temperature for 1 hour. The methyl hydrogen polysiloxane which denaturalized by the phenethyl group and the polyoxyalkylene polymer 70g, without using alpha-methylstyrene, and also same operation was performed, and the methyl hydrogen polysiloxane which denaturalized by the polyoxyethylene group was obtained as viscous liquid. It was 9.3 mmol/g when the SiH value of this polysiloxane was measured.

According to the example 6 of synthetic example 8 composition, the methylhydrogensiloxane

which it was made to react using 47.2 g of alpha-methylstyrene, without using a polyoxyethylene polymer, and also performed same operation and denaturalized was obtained as a viscous liquid object. SiH value was 9.6 mmol/g.

In the 4 mouth flask provided with synthetic example 9 thermometer, the reflux condenser, the dropping funnel, and the agitating motor, 36.9 g of novolac type phenol resin (PMS426), the Gunsei Chemical Industry Co., Ltd. make, OH content 9.71 mmol/g and 160 ml of acetone were put in, and the potassium carbonate 50g was added, stirring. After the allyl star's picture 52g was dropped every in small quantities, it was made to react at 55 \*\* for 6 hours. This was filtered and condensed and it washed in order of alkali and acid, and after adding and stirring the aluminum silicate 7.4g, it filtered and condensed further and the unsaturation group content measured with iodine value acquired the output 40g of 7.3 mmol/g. It was checked that this output is O-arylation novolac type phenol resin by which the hydroxyl group was arylated by measurement of nuclear magnetic resonance.

It heated at 180 \*\* for 3 hours, stirring 40 g of O-arylation novolac type phenol resin obtained in the example 3 of synthetic example 10, composition under a nitrogen atmosphere, and the unsaturation group content measured with iodine value obtained the rearranged product 40g of 7.3 mmol/g. It was checked that this output is C-arylation novolac type phenol resin in which the allyl group carried out the Claisen rearrangement by measurement of nuclear magnetic resonance.

The compound 7.9g compounded in the example 1 of example 1, composition and the 2,2'-diarylbisphenol A 9.2g were mixed, and xylene solution 0.47ml (a platinum atom is used and it is  $6.0 \times 10^{-8}$  mol) of the platinum-vinyl siloxane complex was added, and it mixed further. It was shown that this mixture is almost transparent and both compatibility is good. This mixture was slushed into the mold so that it might be set to 3 mm in thickness, after settling for 3 hours and defoaming at 50 \*\*, was hardened by heating at 150 \*\* for 1 hour, and gave the uniform transparent Plastic solid.

Instead of the example 22,2'-diarylbisphenol A 9.2g, the same operation as Example 1 was performed except having used the mixture of the 2,2'-diarylbisphenol A 7.4g and 1.8 g of bisphenol A diaryl ether. As a result, the mixture was completely transparent, it hardened and the uniform transparent Plastic solid was given.

The same operation as Example 1 was performed except having used the compound 7.9g compounded in the synthetic example 2 instead of the compound 7.9g compounded in the example 1 of comparative example 1 composition. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

The same operation as Example 2 was performed except having used the compound 7.9g compounded in the synthetic example 2 instead of the compound 7.9g compounded in the synthetic example 1 of comparative example 2 composition. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

The same operation as Example 1 was performed using the compound 7.9g compounded in the example 1 of example 3 composition, and the compound 9.2g compounded in the synthetic example 9. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

According to example 4, Example 3, the compound 9.2g compounded in the synthetic example 10 was used instead of the compound compounded in the synthetic example 9, and also the same operation as Example 3 was performed. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

The same operation was performed using the compound 7.7g compounded in the synthetic example 1 according to example 5 instead of the compound 7.9g compounded in the synthetic example 4 instead of the compound 9.2g compounded in the synthetic example 3 instead of the compound 9.20g containing the hydroxyl group manufactured in the example 1 of example 13

instead of the compound compounded in the synthetic example 1 according to example 6 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 7.2g compounded in the synthetic example 5 instead of the compound compounded in the synthetic example 1 according to example 7 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 7.2g compounded in the synthetic example 6 instead of the compound compounded in the synthetic example 1 according to example 8 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 6.6g compounded in the synthetic example 7 instead of the compound compounded in the synthetic example 1 according to comparative example 3 Example 1. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

Same operation was performed using the compound 6.3g compounded in the synthetic example 7 instead of the compound compounded in the synthetic example 1 according to comparative example 4 Example 1. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

According to comparative example 5 Example 1, instead of the compound compounded in the synthetic example 1, 3.9 g of poly methylhydrogensiloxane (KF-99) was used, and same operation was performed. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

According to comparative example 6 Example 1, instead of the compound compounded in the synthetic example 1, 3.9 g of 1, 3, 5, and 7-tetramethyl cyclotetrasiloxane (KF-9902) was used, and same operation was performed. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

Same operation was performed using the compound 7.9g and 240 g of end allyl etharification polypropylene oxide (number average molecular weight 8000 [ about ]) which were compounded in the synthetic example 9 Example 1 according to example 9 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 7.9g, and 30 g of the end allyl esterized phthalic acid / diethylene-glycol copolymers (number average molecular weight 1000 [ about ]) compounded in the synthetic example 10 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

The example 112,2'-diarylbisphenol A 10.8g (0.070 mol of vinyl groups), the compound 9.20g (0.070 mol of SiH groups) containing the hydroxyl group manufactured in the synthetic example 1, and 1.5 g of n-butane were mixed, and it was considered as uniform liquid. It foamed generating heat, when 43 mg of xylene solutions (it is 3.0 % of the weight with a platinum atom) of the platinum-vinyl siloxane were added here and agitation mixing was violently carried out for 10 seconds, and hard foam was obtained. a dimensional change [ as opposed to / settle foam at 23 \*\* for 24 hours, and / immediately after the end of foaming ] — percentage — expressing (contraction is called below) — it was 5% or less. When the cube was cut down from the obtained foam, and weight was measured and having been asked for density, it was 27.5kg/m<sup>3</sup>. It was 85% when the rate of a closed cell was measured according to ASTM-D2856.

Instead of the example 122,2'-diarylbisphenol A 10.8g, The same operation as Example 11 was performed except having used the mixture of the 2,2'-diarylbisphenol A 5.39g (0.035 mol of vinyl groups), and 5.39 g (0.035 mol of vinyl groups) of bisphenol A diaryl ether. Contraction of the obtained foam was 5% or less, and the density of 22.8 kg/m<sup>3</sup> and the rate of a closed cell was 82%.

The same operation as Example 11 was performed except having used the compound 8.64g

which contains the hydroxyl group manufactured in the synthetic example 3 instead of the compound 9.20g containing the hydroxyl group manufactured in the example 1 of example 13

composition. The density of the obtained foam was 27.8 kg/m<sup>3</sup> and the rate of a closed cell was 70%. Instead of the example 142,2'-diarylbisphenol A 10.8g, The same operation as Example 11 was performed except having used the mixture of 4.8 g (0.035 mol of vinyl groups) of O-arylation novolac type phenol resin manufactured in the synthetic example 9, and 4.8 g (0.035 mol of vinyl groups) of C-arylation novolac type phenol resin manufactured in the synthetic example 10.

Contraction of the obtained foam was 5% or less, and the density of 38.5 kg/m<sup>3</sup> and the rate of a closed cell was 60%.

The same operation as Example 11 was performed except having used 3.6 g (0.025 mol) of 2-ethylhexanoic acid instead of 1.5 g of 15n of examples-butane. The density of foam was 45.9 kg/m<sup>3</sup> and the rate of a closed cell was 61%.

Instead of the compound 9.20g containing the hydroxyl group manufactured in the example 1 of example 16 composition. The same operation as Example 11 was performed except having used the compound 4.60g (0.035 mol of SiH groups) containing the hydroxyl group manufactured in the synthetic example 1, and the mixture with 5.21 g (0.035 mol of SiH groups) of denaturation methyl hydrogen polysiloxane manufactured in the synthetic example 6. The density of the obtained foam was 24.3 g/m<sup>3</sup> and the rate of a closed cell was 72%.

The example 172,2'-diarylbisphenol A 10.8g (0.070 mol of vinyl groups), the compound 9.20g (0.070 mol of SiH groups) containing the hydroxyl group manufactured in the synthetic example 4, and HFC245fa3.0g were mixed, and it was considered as uniform liquid. It foamed generating heat, when the platinum-vinyl siloxane solution was added like Example 11 and agitation mixing was violently carried out for 10 seconds, and hard foam was obtained. Contraction of the obtained foam was 5 to 10%, and the density of 30.5 kg/m<sup>3</sup> and the rate of a closed cell was 85%.

The same operation as Example 11 was performed except having used 8.43 g of denaturation siloxanes manufactured in the synthetic example 5 instead of the compound containing the hydroxyl group manufactured in the example 4 of example 18 composition. Although contraction of the obtained foam was 30%, density was 50 kg/m<sup>3</sup> and the rate of a closed cell was 60%. The same operation as Example 11 was performed except having used 9.2 g of denaturation siloxanes manufactured in the synthetic example 6 instead of the compound containing the hydroxyl group manufactured in the example 4 of example 19 composition. Although contraction of the obtained foam was 30%, density was 50 kg/m<sup>3</sup> and the rate of a closed cell was 60%. 280 g of polypropylene oxide used in example 19, Example 9, the compound 9.20g containing the hydroxyl group manufactured in the synthetic example 4, and HFC245fa10.0g were mixed, and it was considered as uniform liquid. It foamed generating heat, when the platinum-vinyl siloxane solution was added like Example 11 and agitation mixing was violently carried out for 10 seconds, and elastic foam was obtained. The density of the obtained foam was 200 kg/m<sup>3</sup>. The end ally esterized phthalic acid / diethylene-glycol copolymer 35g used in example 20 Example 10, the compound 9.20g containing the hydroxyl group manufactured in the synthetic example 4, and HFC245fa8.0g were mixed, and it was considered as uniform liquid. It foamed generating heat, when the platinum-vinyl siloxane solution was added like Example 11 and agitation mixing was violently carried out for 10 seconds, and elastic foam was obtained. The density of the obtained foam was 70 kg/m<sup>3</sup>.

Instead of the compound containing the hydroxyl group manufactured in the example 1 of comparative example 7 composition, the same operation as Example 11 was performed except having used 4.20 g of 1, 3, 5, and 7-tetramethyl cyclotetrasiloxane. As a result, the allyl compound and the SiH compound did not dissolve and did not form foam.

The same operation as Example 11 was performed except having used 7.29 g of denaturation poly methylhydrogensiloxane manufactured in the synthetic example 7 instead of the compound containing the hydroxyl group which \*\*\*\*\*\*(ed) example of comparative example 8 composition 1. The obtained foam was 80kg/m<sup>3</sup>, and the rate of a closed cell was 30%.

composition. The density of the obtained foam was 27.8 kg/m<sup>3</sup> and the rate of a closed cell was 70%. Instead of the example 142,2'-diarylbisphenol A 10.8g, The same operation as Example 11 was performed except having used the mixture of 4.8 g (0.035 mol of vinyl groups) of O-arylation novolac type phenol resin manufactured in the synthetic example 9, and 4.8 g (0.035 mol of vinyl groups) of C-arylation novolac type phenol resin manufactured in the synthetic example 10.

Contraction of the obtained foam was 5% or less, and the density of 38.5 kg/m<sup>3</sup> and the rate of a closed cell was 60%.

The same operation as Example 11 was performed except having used 3.6 g (0.025 mol) of 2-ethylhexanoic acid instead of 1.5 g of 15n of examples-butane. The density of foam was 45.9 kg/m<sup>3</sup> and the rate of a closed cell was 61%.

Instead of the compound 9.20g containing the hydroxyl group manufactured in the example 1 of example 16 composition. The same operation as Example 11 was performed except having used the compound 4.60g (0.035 mol of SiH groups) containing the hydroxyl group manufactured in the synthetic example 1, and the mixture with 5.21 g (0.035 mol of SiH groups) of denaturation methyl hydrogen polysiloxane manufactured in the synthetic example 6. The density of the obtained foam was 24.3 g/m<sup>3</sup> and the rate of a closed cell was 72%.

The example 172,2'-diarylbisphenol A 10.8g (0.070 mol of vinyl groups), the compound 9.20g (0.070 mol of SiH groups) containing the hydroxyl group manufactured in the synthetic example 4, and HFC245fa3.0g were mixed, and it was considered as uniform liquid. It foamed generating heat, when the platinum-vinyl siloxane solution was added like Example 11 and agitation mixing was violently carried out for 10 seconds, and hard foam was obtained. Contraction of the obtained foam was 5 to 10%, and the density of 30.5 kg/m<sup>3</sup> and the rate of a closed cell was 85%.

The same operation as Example 11 was performed except having used 8.43 g of denaturation siloxanes manufactured in the synthetic example 5 instead of the compound containing the hydroxyl group manufactured in the example 4 of example 18 composition. Although contraction of the obtained foam was 30%, density was 50 kg/m<sup>3</sup> and the rate of a closed cell was 60%. The same operation as Example 11 was performed except having used 9.2 g of denaturation siloxanes manufactured in the synthetic example 6 instead of the compound containing the hydroxyl group manufactured in the example 4 of example 19 composition. Although contraction of the obtained foam was 30%, density was 50 kg/m<sup>3</sup> and the rate of a closed cell was 60%. 280 g of polypropylene oxide used in example 19, Example 9, the compound 9.20g containing the hydroxyl group manufactured in the synthetic example 4, and HFC245fa10.0g were mixed, and it was considered as uniform liquid. It foamed generating heat, when the platinum-vinyl siloxane solution was added like Example 11 and agitation mixing was violently carried out for 10 seconds, and elastic foam was obtained. The density of the obtained foam was 200 kg/m<sup>3</sup>. The end ally esterized phthalic acid / diethylene-glycol copolymer 35g used in example 20 Example 10, the compound 9.20g containing the hydroxyl group manufactured in the synthetic example 4, and HFC245fa8.0g were mixed, and it was considered as uniform liquid. It foamed generating heat, when the platinum-vinyl siloxane solution was added like Example 11 and agitation mixing was violently carried out for 10 seconds, and elastic foam was obtained. The density of the obtained foam was 70 kg/m<sup>3</sup>.

Instead of the compound containing the hydroxyl group manufactured in the example 1 of comparative example 7 composition, the same operation as Example 11 was performed except having used 4.20 g of 1, 3, 5, and 7-tetramethyl cyclotetrasiloxane. As a result, the allyl compound and the SiH compound did not dissolve and did not form foam.

The same operation as Example 11 was performed except having used 7.29 g of denaturation poly methylhydrogensiloxane manufactured in the synthetic example 7 instead of the compound containing the hydroxyl group which \*\*\*\*\*\*(ed) example of comparative example 8 composition 1. The obtained foam was 80kg/m<sup>3</sup>, and the rate of a closed cell was 30%.

The same operation as Example 11 was performed except having used 7.53 g of denaturation poly methylhydrogensiloxane manufactured in the synthetic example 8 instead of the compound containing the hydroxyl group manufactured in the example 1 of comparative example 9 composition. It was 33 kg/m<sup>3</sup> when asked for the density of the obtained foam. It was 10% when the rate of a closed cell was measured.

Industrial applicability According to this invention, a polar high carbon-carbon double bond content organic system compound can provide the hardenability constituent and fizz resin composition using the hardening agent which has sufficient compatibility, and this hardening agent.

Since the hardenability constituent using the hardening agent of this invention is excellent in a mechanical strength and it excels also in appearance, such as transparency, the use in particular is not limited but can be used for a general large use.

As the example, for example Coating agents, such as sealing materials, such as electrical machinery and electronic parts, a under body coat, structural water proof coating for cars, Resin modifiers, such as various paints, such as various molding materials, such as a charge of a gasket material, a sealing material, rubber, resin, liquefied, powder state, adhesives, or a physical properties improving agent, a compatibilizer, etc., etc. are mentioned.

According to the fizz resin composition of this invention, ordinary temperature or foam with expansion ratio under low-temperature heating, can carry out foam curing comparatively, and high and a rate of a closed cell high moreover is obtained. Therefore, since foam with sufficient insulation efficiency can be obtained with the high rate of a closed cell while being able to lower the price per unit volume with high expansion ratio, it is widely applicable to various uses, such as noise control, heat insulation, water cutoff, airtightness, damping, protection, a cushion, and an ornament.

Although not necessarily limited, especially as the example The cushioning material for vehicles for example, A ceiling material, door trim central supply, a floor cushion damping sound-absorbing material, car air conditioner thermal insulation, The air-seal material for dampers, a water blocking material, a gasket, an air filter, Center pillar garnish, a headliner, a quarter trim, A dust cover, the safety form in a fuel tank, an oil filter, Flexible freight containers, a crush pad, a sun visor, a headrest, An insulator, a dashboard, a door panel, a pillar, a console box, Thermal insulation, such as a energy-absorbing bumper, a refrigerator car, an insulated truck, a tank lorry vehicle, and a reef container vehicle, Thermal insulation for marine vessels, such as a guard sound insulating material, a buoyancy material an FRP board core, a buoy, etc., Cushioning materials [such as furniture,], such as a cushioning material for bed and bedding, a packing material, etc., The filter for electrical and electric equipment, sound absorption thermal insulation, a printer sound absorbing material, head telephone year putt, etc., In the shock absorbing material for a package, and the object for construction, heat insulation incubation core materials, such as core materials, such as covering of the thermal insulation of a roof, a ceiling, a wall, and a floor, a city water pipe, etc., a door panel, a sizing panel metal, a core material of a partition panel, a tatami and a bran core material and a tub, a bond, A sealing material, adhesives, a system ceiling heat insulation panel, a roof insulation waterproof material. The tank, piping insulation material, etc. of airtight thermal insulation, such as a cold storage warehouse and an airtight warehouse, and a plant, In the object for household appliances, consumer-goods uses, such as thermal insulation, such as a refrigerator, a freezer, and an electronic jar, the preventing-dew-condensation material of an air conditioner, sporting goods and medical supplies and the puff for makeup, shoulder putt, slippers, sandals, a needle point holder, and a toy, are mentioned.

A fizz resin composition of this invention, foam using this, and a manufacturing method for the same are applicable to templating of the article shape in a casting method, model sample production from a mold, accessories production, etc.

[Translation done.]

## \* NOTICES \*

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- This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## EXAMPLE

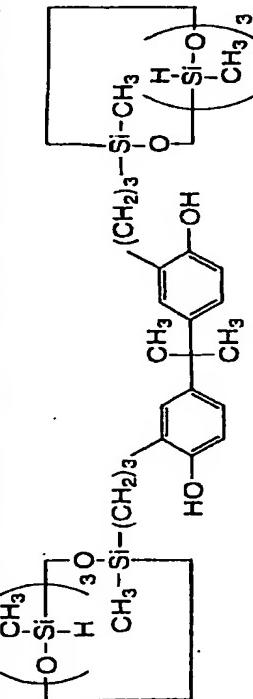
## [Example]

Next, an example explains this invention still more concretely. However, this invention is not limited to the following examples.

1504g of 1,3,5,7-tetramethyl cyclotetrasiloxane (product [ made from Shin-etsu Chemicals ] KF9902) and 500 ml of toluene were put into the 4 poem round bottom flask of 3L provided with synthetic example 1 thermometer, the agitating equipment child, the tap funnel, and the capacitor under a nitrogen atmosphere. Xylene solution 47.2ml (a platinum atom is used and it is  $6.2 \times 10^{-6}$  mol) of the bottom of stirring and a platinum-vinyl siloxane complex was dissolved in 20 ml of toluene at the room temperature, and it added. What warmed at 70 \*\* and dissolved with 2,2'-diarylbisphenol A 192g in 200 ml of toluene under stirring was added from the tap funnel over 30 minutes. The tap funnel was washed with 30 ml of toluene after the end of addition.

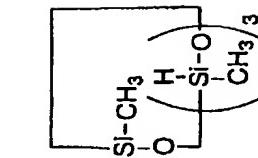
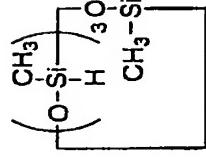
After stirring the obtained solution at 70 \*\* for 2 hours, 16.7 mg of benzothiazole was added.

Toluene and unreacted tetramethyl cyclotetrasiloxane were distilled off under decompression, and the consistency brown [ 470 g of ] fluid was obtained. It is a formula by analysis of the nuclear magnetic resonance of this thing, mass analysis, infrared spectroscopic analysis, etc.:



It came out and was identified a compound expressed.

500g of 1,3,5,7-tetramethyl cyclotetrasiloxane and 150 ml of toluene were put into the 4-poem round bottom flask of 2L provided with synthetic example 2 thermometer, an agitating equipment child, a tap funnel, and a capacitor under a nitrogen atmosphere. Xylene solution 15.6ml of the bottom of stirring and a platinum-vinyl siloxane complex was dissolved in 20 ml of toluene at a room temperature, and it added. What warmed at 70 \*\* and dissolved 64.1 g of bisphenol A diaryl ether in 60 ml of toluene under stirring was added from a tap funnel over 30 minutes. A tap funnel was washed with 20 ml of toluene after an end of addition. After stirring an obtained solution at 70 \*\* for 2 hours, 4.7 mg of benzothiazole was added. Toluene and unreacted tetramethyl cyclotetrasiloxane were distilled off under decompression, and the 165 g a little consistency fluid of thin yellow was obtained. It is a formula by analysis of this thing nuclear magnetic resonance, mass analysis, infrared spectroscopic analysis, etc.:



It came out and was identified a compound expressed.

A condenser tube and a thermometer which attached a method tap of three to a rabbie, a dropping funnel, and the upper part were set to a 4 mouth flask of 31 l. of synthetic examples. Xylene solution 241ml of 1, 3, 5, 120 g of 7-tetramethyl cyclotetrasiloxane, and a platinum-vinyl siloxane complex and 120 ml of toluene were put into this flask. Mixed liquor was heated at 80 \*\* and O-allylphenol 67.0g (0.50 mol) was dropped over 20 minutes from a dropping funnel. It agitated as it is at 80 \*\* for 2 hours.

It checked that a peak of a vinyl group had disappeared a reaction mixture by measurement of nuclear magnetic resonance, and after cooling, the activated carbon 10g was added and it agitated at a room temperature for 1 hour. Methyl hydrogen cyclosiloxane which denaturalized by 3-(2-hydroxyphenyl) propyl group was obtained a little as viscous liquid by filtering a mixture and condensing filtrate. It was 8.1 mmol/g when SiH value of this polysiloxane was measured.

A condenser tube, a thermometer which connected a method tap of three to synthetic example 4 dropping funnel and the upper part. In the 4 Thu mouth flask which connected a mechanical stirrer, 60.1 g of 1,3,5,7-tetramethyl cyclotetrasiloxane was put in, and it heated at 40 \*\*, passing oxygen / nitrogen mixed gas (1% of oxygen content) from a method tap of three. 6.5 mg of Pt-vinyl siloxanes (3% xylene solution) were put in, the O,O'-diarylbisphenol A 30.8g was dropped from a dropping funnel, and an end trickled after that 8.1 g of polyethylene oxide polymers (number average molecular weight 400) replaced by allyl group and a methyl group.

After agitating at 40 degrees then for 1 hour and completing a reaction, benzothiazole was added as stabilizer. A little \*\*\*\*\* transparent liquid was obtained by heating under decompression of a reaction mixture and distilling off volatile matter content.

A condenser tube and a thermometer which attached a three-way cock to a rabbie, a dropping funnel, and the upper part were set to a 4 mouth flask of 51 l. of synthetic examples. Xylene solution 241ml of 120 g of 1,3,5,7-tetramethyl cyclotetrasiloxane and a platinum-vinyl siloxane complex was put into this flask. Mixed liquor was heated at 40 \*\* and 11.8 g (0.10 mol) of alpha-methylstyrene was dropped over 5 minutes from a dropping funnel. It checks that a peak of a vinyl group has disappeared a reaction mixture by  $^1\text{H-NMR}$  after 30-minute churning. Next, another [ a methyl group and ] end trickled 70 g (0.20 mol of allyl groups) of ethylene oxide polymers (number average molecular weight 350) which denaturalized, respectively over 10 minutes by an allyl group, and a piece end agitated as it is at 80 \*\* after an end for 2 hours.

It checked that a peak of a vinyl group had disappeared a reaction mixture by  $^1\text{H-NMR}$ , and after cooling, the activated carbon 10g was added and it agitated at a room temperature for 1 hour. A mixture was filtered and cyclotetrasiloxane which denaturalized by phenethyl group and a polyoxyalkylene group was obtained as viscous liquid. It was 8.3 mmol/g when SiH value of this polysiloxane was measured.

According to the example 4 of synthetic example 6 composition, xylene solution 241ml of 120 g of polyorganohydrogen siloxanes (product [ made from Shin-etsu Chemicals ] KF-99), 120 ml of toluene, and a platinum-vinyl siloxane complex was put in instead of 1,3,5,7-tetramethyl cyclotetrasiloxane. Mixed liquor was heated at 80 \*\*, and like the synthetic example 5, 11.8 g of alpha-methylstyrene and the ethylene oxide polymer 70g were dropped over 10 minutes from a dropping funnel, and it agitated as it is at 80 \*\* after an end for 2 hours.

It checked that the peak of the vinyl group had disappeared the reaction mixture by <sup>1</sup>H-NMR, and after cooling, the activated carbon 10g was added and it agitated at the room temperature for 1 hour. The methyl hydrogen polysiloxane which denaturalized by the phenethyl group and the polyoxyalkylene group was obtained as viscous liquid by filtering a mixture and condensing filtrate. It was 8.3 mmol/g when the SiH value of this polysiloxane was measured.

According to the example 6 of synthetic example 7 composition, it was made to react only using the polyoxyethylene polymer 70g, without using alpha-methylstyrene, and also same operation was performed, and the methyl hydrogen polysiloxane which denaturalized by the polyoxyethylene group was obtained as viscous liquid. It was 9.3 mmol/g when the SiH value of this polysiloxane was measured.

According to the example 6 of synthetic example 8 composition, the methylhydrogensiloxane which it was made to react using 47.2 g of alpha-methylstyrene, without using a polyoxyethylene polymer, and also performed same operation and denaturalized was obtained as a viscous liquid object. SiH value was 9.6 mmol/g.

In the 4 mouth flask provided with synthetic example 9 thermometer, the reflux condenser, the dropping funnel, and the agitating motor. 36.9g of novolac type phenol resin (PSM4261, the Gunsei Chemical Industry Co., Ltd. make, OH content 9.71 mmol/g) and 160 ml of acetone were put in, and the potassium carbonate 50g was added, stirring. After the allyl star's picture 52g was dropped every in small quantities, it was made to react at 55 \*\* for 6 hours. This was filtered and condensed and it washed in order of alkali and acid, and after adding and stirring the aluminum silicate 7.4g, it filtered and condensed further and the unsaturation group content measured with iodine value acquired the output 40g of 7.3 mmol/g. It was checked that this output is O-arylation novolac type phenol resin by which the hydroxyl group was arylated by measurement of nuclear magnetic resonance.

It heated at 180 \*\* for 3 hours, stirring 40 g of O-arylation novolac type phenol resin obtained in the example 3 of synthetic example 10 composition under a nitrogen atmosphere, and the unsaturation group content measured with iodine value obtained the rearranged product 40g of 7.3 mmol/g. It was checked that this output is C-arylation novolac type phenol resin in which the allyl group carried out the Claisen rearrangement by measurement of nuclear magnetic resonance.

The compound 7.9g compounded in the example 1 of example 1 composition and the 2,2'-diarylbisphenol A 9.2g were mixed, and xylene solution 0.47ml (a platinum atom is used, and it is 6.0x10<sup>-8</sup> mol) of the platinum-vinyl siloxane complex was added, and it mixed further. It was shown that this mixture is almost transparent and both compatibility is good. This mixture was slushed into the mold so that it might be set to 3mm in thickness, after settling for 3 hours and defoaming at 50 \*\*, was hardened by heating at 150 \*\* for 1 hour, and gave the uniform transparent Plastic solid.

Instead of the example 222'-diarylbisphenol A 9.2g, the same operation as Example 1 was performed except having used the mixture of the 2,2'-diarylbisphenol A 7.4g and 1.8 g of bisphenol A diaryl ether. As a result, the mixture was completely transparent, it hardened and the uniform transparent Plastic solid was given.

The same operation as Example 1 was performed except having used the compound 7.9g compounded in the synthetic example 2 instead of the compound 7.9g compounded in the example 1 of comparative example 1 composition. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

The same operation as Example 2 was performed except having used the compound 7.9g compounded in the synthetic example 2 instead of the compound 7.9g compounded in the example 1 of comparative example 2 composition. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

The same operation as Example 1 was performed using the compound 9.2g compounded in the example 1 of example 3 composition, and the compound 9.2g compounded in the synthetic

example 9. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

According to example 4 Example 3, the compound 9.2g compounded in the synthetic example 10 was used instead of the compound compounded in the synthetic example 9, and also the same operation as Example 3 was performed. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 7.7g compounded in the synthetic example 3 instead of the compound compounded in the synthetic example 1 according to example 5 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 7.9g compounded in the synthetic example 4 instead of the compound compounded in the synthetic example 1 according to example 6 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 7.9g compounded in the synthetic example 5 instead of the compound compounded in the synthetic example 1 according to example 7 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 7.2g compounded in the synthetic example 6 instead of the compound compounded in the synthetic example 1 according to example 7 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 7.2g compounded in the synthetic example 5 instead of the compound compounded in the synthetic example 1 according to example 8 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 6.6g compounded in the synthetic example 7 instead of the compound compounded in the synthetic example 1 according to comparative example 3 Example 1. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

Same operation was performed using the compound 6.3g compounded in the synthetic example 7 instead of the compound compounded in the synthetic example 1 according to comparative example 4 Example 1. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

According to comparative example 5 Example 1, instead of the compound compounded in the synthetic example 1, 3.9 g of 1, 3, 5, and -tetramethyl cyclotetrasiloxane (KF-9902) was used, and same operation was performed. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

According to comparative example 6 Example 1, instead of the compound compounded in the synthetic example 1, 3.9 g of 1, 3, 5, and -tetramethyl cyclotetrasiloxane (KF-9902) was used, and same operation was performed. As a result, the mixture became cloudy and did not dissolve. Even if heated, what was obtained did not give an uneven and good hardened material.

Even if heated, what was obtained did not give an uneven and good hardened material.

Same operation was performed using the compound 7.9g and 240 g of end allyl esterification

polypropylene oxide (number average molecular weight 8000 [ about ]) which were compounded in the synthetic example 1 according to example 9 Example 1. The compatibility of a mixture is

good and the uniform transparent hardened material was obtained by heating.

Same operation was performed using the compound 7.9g, and 30 g of the end allyl esterized phthalic acid / diethylene-glycol copolymers (number average molecular weight 1000 [ about ]) compounded in the synthetic example 1 according to example 10 Example 1. The compatibility of a mixture is good and the uniform transparent hardened material was obtained by heating.

The example 112,2'-diarylbisphenol A 10.8g (0.070 mol of vinyl groups), the compound 9.20g (0.070 mol of SiH groups) containing a hydrosilyl group manufactured in the synthetic example 1, and 1.5 g of n-butane were mixed, and it was considered as uniform liquid. It foamed generating heat, when 43 mg of xylene solutions (it is 30 % of the weight with a platinum atom) of a platinum-vinyl siloxane were added here and agitation mixing was violently carried out for 10 seconds, and hard foam was obtained. a dimensional change [ as opposed to / settle foam at 23 \*\* for 24 hours, and / immediately after an end of foaming ] — percentage — expressing (contraction is called below) — it was 5% or less. When a cube was cut down from obtained

foam, and weight was measured and having been asked for density, it was  $27.5\text{kg}/[\text{m}]^3$ . It was 85% when a rate of a closed cell was measured according to ASTM-D2856. Instead of the example 122,2'-diarylbisphenol A 10.8g, The same operation as Example 11 was performed except having used a mixture of the 2,2'-diarylbisphenol A 5.39g (0.035 mol of vinyl groups), and 5.39 g (0.035 mol of vinyl groups) of bisphenol A diaryl ether. Contraction of obtained foam was 5% or less, and density of  $22.8\text{kg}/\text{m}^3$  and a rate of a closed cell was 82%. The same operation as Example 11 was performed except having used the compound 8.64g which contains a hydroxyl group manufactured in the synthetic example 3 instead of the compound 9.20g containing a hydroxyl group manufactured in the example 1 of example 13 composition. Density of obtained foam was  $27.8\text{kg}/\text{m}^3$  and a rate of a closed cell was 70%.

Instead of the example 14,2'-diarylbisphenol A 10.8g, The same operation as Example 11 was performed except having used a mixture of 4.8 g (0.035 mol of vinyl groups) of O-arylation novolac type phenol resin manufactured in the synthetic example 9, and 4.8 g (0.035 mol of vinyl groups) of C-arylation novolac type phenol resin manufactured in the synthetic example 10. Contraction of obtained foam was 5% or less, and density of  $38.5\text{kg}/\text{m}^3$  and a rate of a closed cell was 60%.

The same operation as Example 11 was performed except having used 3.6 g (0.025 mol) of 2-ethylhexanoic acid instead of 1.5 g of 15n. of examples-butane. Density of foam was  $45.9\text{kg}/\text{m}^3$  and a rate of a closed cell was 61%. Instead of the compound 9.20g containing a hydroxyl group manufactured in the example 1 of example 16 composition, The same operation as Example 11 was performed except having used the compound 4.60g (0.035 mol of SiH groups) containing a hydroxyl group manufactured in the synthetic example 1, and a mixture with 5.21 g (0.035 mol of SiH groups) of denaturation methyl hydrogen polysiloxane manufactured in the synthetic example 6. Density of obtained foam was  $24.3\text{g}/\text{m}^3$  and a rate of a closed cell was 72%.

The example 172,2'-diarylbisphenol A 10.8g (0.070 mol of vinyl groups), the compound 9.20g (0.070 mol of SiH groups) containing a hydroxyl group manufactured in the synthetic example 4, and HFC245fa3.0g were mixed, and it was considered as uniform liquid. It foamed generating heat, when a platinum-vinyl siloxane solution was added like Example 11 and agitation mixing was violently carried out for 10 seconds, and hard foam was obtained. Contraction of obtained foam was 5 to 10%, and density of  $30.5\text{kg}/\text{m}^3$  and a rate of a closed cell was 85%.

The same operation as Example 11 was performed except having used 8.43 g of denaturation siloxanes manufactured in the synthetic example 5 instead of a compound containing a hydroxyl group manufactured in the example 4 of example 18 composition. Although contraction of obtained foam was  $50\text{ kg}/\text{m}^3$  and a rate of a closed cell was 60%.

The same operation as Example 11 was performed except having used 9.2 g of denaturation siloxanes manufactured in the synthetic example 6 instead of a compound containing a hydroxyl group manufactured in the example 4 of example 19 composition. Although contraction of obtained foam was 30%, density was  $50\text{ kg}/\text{m}^3$  and a rate of a closed cell was 60%.

In example 19, Example 9, the compound 9.20g containing a hydroxyl group manufactured in the synthetic example 4, and HFC245fa10.0g were mixed, and it was considered as uniform liquid. It foamed generating heat, when a platinum-vinyl siloxane solution was added like Example 11 and agitation mixing was violently carried out for 10 seconds, and elastic foam was obtained. Density of obtained foam was  $200\text{ kg}/\text{m}^3$ .

The end ally ester-ized phthalic acid / diethylene-glycol copolymer 35g used in example 20, Example 10, the compound 9.20g containing a hydroxyl group manufactured in the synthetic example 4, and HFC245fa8.0g were mixed, and it was considered as uniform liquid. It foamed generating heat, when a platinum-vinyl siloxane solution was added like Example 11 and agitation mixing was violently carried out for 10 seconds, and elastic foam was obtained. Density of obtained foam was  $70\text{ kg}/\text{m}^3$ .

Instead of a compound containing a hydroxyl group manufactured in the example 1 of

comparative example 7 composition, the same operation as Example 11 was performed except having used 4.20 g of 1, 3, 5, and 7-tetramethyl cyclotetrasiloxane. As a result, an allyl compound and a SiH compound did not dissolve and did not form foam.

The same operation as Example 11 was performed except having used 7.29 g of denaturation poly methylhydrogensiloxane manufactured in the synthetic example 7 instead of the compound containing the hydroxyl group which \*\*\*\*\*led example of comparative example 8 composition

1. The obtained foam was  $80\text{kg}/[\text{m}]^3$ , and the rate of a closed cell was 30%. The same operation as Example 11 was performed except having used 7.53 g of denaturation poly methylhydrogensiloxane manufactured in the synthetic example 8 instead of the compound containing the hydroxyl group manufactured in the example 1 of comparative example 9 composition. It was  $33\text{ kg}/\text{m}^3$  when asked for the density of the obtained foam. It was 10% when the rate of a closed cell was measured.

Industrial applicability According to this invention, a polar high carbon-carbon double bond content organic system compound can provide the hardenability constituent and fizz resin composition using the hardening agent which has sufficient compatibility, and this hardening agent.

Since the hardenability constituent using the hardening agent of this invention is excellent in a mechanical strength and it excels also in appearance, such as transparency, the use in particular is not limited but can be used for a general large use.

As the example, for example Coating agents, such as sealing materials, such as electrical machinery and electronic parts, a under body coat, structural water proof coating for cars, Resin modifiers, such as various paints, such as various molding materials, such as a charge of a gasket material, a sealing material, rubber-, resin-, liquefied, powder state, adhesives, or a physical properties improving agent, a compatibilizer, etc., etc. are mentioned.

According to the fizz resin composition of this invention, ordinary temperature or foam with expansion ratio under low-temperature heating, can carry out foam curing comparatively, and high and a rate of a closed cell high moreover is obtained. Therefore, since foam with sufficient insulation efficiency can be obtained with a high rate of a closed cell while being able to lower a price per unit volume with high expansion ratio, it is widely applicable to various uses, such as noise control, heat insulation, water cutoff, airtightness, damping, protection, a cushion, and an ornament.

Although not necessarily limited especially as the example A cushioning material for vehicles for example, A ceiling material, door trim central supply, a floor cushion damping sound-absorbing material, car air conditioner thermal insulation, Air-seal material for dampers, a water blocking material, a gasket, an air filter, Center pillar garnish, a headliner, a quarter trim, A dust cover, safety form in a fuel tank, an oil filter, Flexible freight containers, a crush pad, a sun visor, a headrest, An insulator, a dashboard, a door panel, a pillar, a console box, Thermal insulation, such as a energy-absorbing bumper, a refrigerator car, an insulated truck, a tank lorry vehicle, and a reefar container vehicle. Thermal insulation for marine vessels, such as a guard sound insulating material, a buoyancy material, an FRP board core, a buoy, etc., Cushioning materials [ such as furniture, ], such as a cushioning material for bed and bedding, a packing material, etc., A filter for electrical and electric equipment, sound absorption thermal insulation, a printer sound-absorbing material, hand telephone year putt, etc., In shock absorbing material for a package, and an object for construction, heat insulation incubation core materials, such as core materials, such as covering of thermal insulation of a roof, a ceiling, a wall, and a floor, a city water pipe, etc., a door panel, a sizing panel, metal, a sizing panel, a core material of a partition panel, a tatami and a bran core material, and a tub, a bond, A sealing material, adhesives, a system ceiling heat insulation panel, a roof insulation waterproof material, A tank, piping insulation material, etc. of airtight thermal insulation, such as a cold storage warehouse and an airtight warehouse, and a plant, in an object for household appliances, consumer goods uses, such as thermal insulation, such as a refrigerator, a freezer, and an electronic jar, preventing-dew-condensation material of an air conditioner, sporting goods and medical supplies and a puff for makeup, shoulder putt, slippers, sandals, a needle point holder, and a toy, are mentioned.

A fizz resin composition of this invention, foam using this, and a manufacturing method for the same are applicable to templating of article shape in a casting method, model sample production from a mold, accessories production, etc.

[Translation done.]

## \* NOTICES \*

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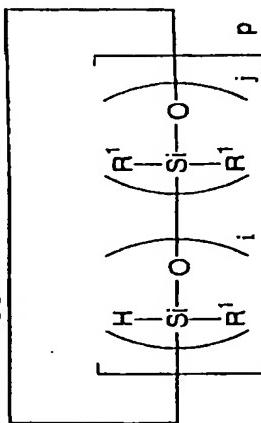
- This document has been translated by computer. So the translation may not reflect the original precisely.
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## CLAIMS

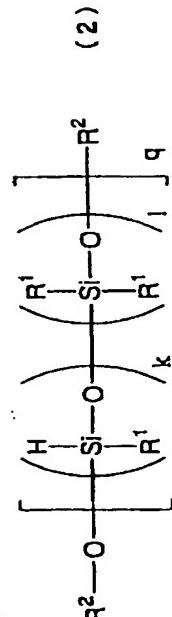
## [Claim(s)]

[Claim 1] It is a hardening agent which stiffens an organic compound which contains at least one carbon-carbon double bond in a molecule — an organic system hardening agent, wherein compatibility with an organic compound containing said carbon-carbon double bond is good.

[Claim 2](a) A following general formula (1)



(R<sup>1</sup>) expresses a basis as which a hydrogen atom and a carbon number are chosen from an organic group of monovalence of 1~20 among a formula (1), and each R<sup>1</sup> may be the same or may differ.) i=2 and j are 0 or a positive number, and p>=1, and i, j, and p are numbers with which it is satisfied of 3 <= {i+j} xp <=50.  
An annular oligo siloxane and/or a following general formula (2) with which it is come out and expressed



the inside of a formula (2), and R<sup>1</sup> — the above — the same — R<sup>2</sup>. A hydrogen atom, -Si(CH<sub>3</sub>)<sub>2</sub>-H, and a carbon number express a basis chosen from an organic group of monovalence of 1~20, and each R<sup>2</sup> may be the same or may differ. k=2 and l are 0 or a positive number, and q>=1, and k, l, and q are numbers with which it is satisfied of 2 <= {l+1} xq <=50.  
A chain polysiloxane come out of and expressed, and the (b) following general formula (3)



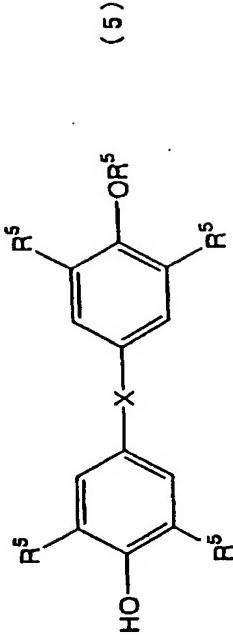
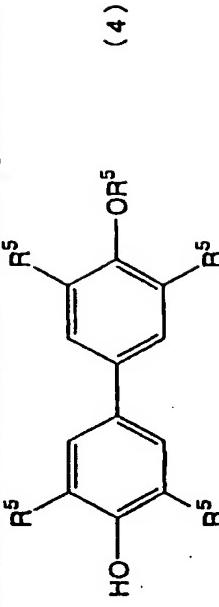
(m and n express the number of 1~3 independently among a formula (3), respectively, and p expresses the number of 0~2.) R<sup>3</sup> expresses an organic group of monovalence of the carbon numbers 1~25 containing one or more carbon-carbon double bonds, and when m is two or more, each R<sup>3</sup> may be the same or may differ. R<sup>4</sup> expresses a basis of monovalence chosen from a halogen atom, an alkoxy group of the carbon numbers 1~6, and an organic group of monovalence of the carbon numbers 1~25, and when p is 2, each R<sup>4</sup> may be the same or may differ.

A hardening agent given in the 1st paragraph of a claim which comes out, makes a compound which has one or more carbon-carbon double bonds and one or more phenolic hydroxyl groups react to intramolecular expressed, and is obtained.

[Claim 3] A hardening agent given in the 2nd paragraph of a claim said j and/or given l are 0.

[Claim 4] A hardening agent given [ said given i is a number with which it is satisfied of 3 <= i <=7 ] in the 3rd paragraph of a claim said given k is a number with which it is satisfied of 2 <= k <=10.

[Claim 5] as the aforementioned (b) ingredient — a following general formula (4) — or (5)



(R<sup>5</sup>) expresses an organic group of monovalence of the carbon numbers 1~10 containing a hydrogen atom or one or more carbon-carbon double bonds among a formula (4) and a formula (5), and each R<sup>5</sup> may be the same or may differ.) The inside of a formula (5) and X are -CH<sub>2</sub>-,-C(CH<sub>3</sub>)<sub>2</sub>-,-CH(CH<sub>3</sub>)<sub>2</sub>-,-C(CF<sub>3</sub>)<sub>2</sub>-,-CO-, -SO<sub>2</sub>-, -O-, or a formula;

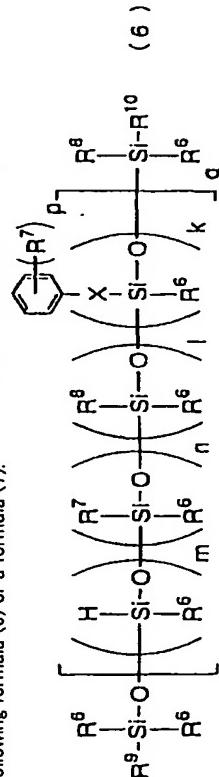


A substituent of bivalence which comes out and is chosen from a basis expressed is shown.  
A hardening agent given in any 1 paragraph of the 2-4th paragraphs of a claim that come out and are characterized by containing a compound which has one or more carbon-carbon double bonds and one or more phenolic hydroxyl groups in intramolecular expressed.

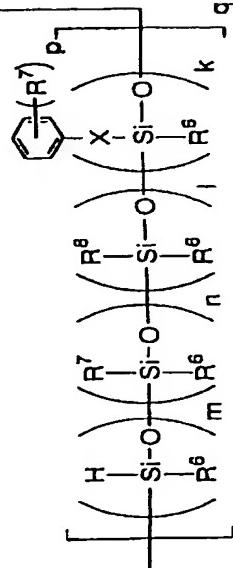
[Claim 6] (i) The chain and/or annular ORGANO hydrogen siloxane whose number of silicon atoms in one molecule is 3-10. (ii) A compound which has a functional group which can react to a hydroxyl group of said (i) ingredient in [ two or more ] one molecule. And a hardening agent given in the 1st paragraph of a claim being the compound in which it was obtained by making an organic compound which contains a functional group which can react to a hydroxyl group of a (iii) aforementioned (i) ingredient in [ one ] one molecule react, and a hydroxyl group of (i) ingredient origin remained on parenthesis.

[Claim 7] A hardening agent given in the 1st paragraph of a claim having the structure shown by a following formula (6) or a formula (7)

given in any 1 paragraph of the 1st paragraph of a claim – the 7th paragraph.  
[Claim 11](C) A hardenability constituent given in the 10th paragraph of a claim containing a hydroxylation catalyst further.  
[Claim 12]The 10th paragraph of a claim or a fizz resin composition given in the 11th paragraph in which a molecular skeleton of an organic compound of the aforementioned (A) ingredient consists only of carbon, oxygen, hydrogen, nitrogen, sulfur, and any one or more sorts of elements of the halogen.  
[Claim 13]Organic compounds of the aforementioned (A) ingredient are a following general formula (B) =  $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{R}_5\text{R}_6\text{R}_7\text{R}_8\text{R}_9\text{R}_{10}$ .



$(m)=2$ ,  $n=0$ ,  $l$ ,  $q=1$ , and  $p$  are an integer of 0-5, and  $10=(m+n+l+k)$   $xq<=80$  among a formula (6), and  $R^6$  and  $R^7$ ) A molecular weight shows polyoxyalkylene chain of 100-10,000, and, as for a univalent substituent of the carbon numbers 0-6, and  $R^8$ ,  $R^9$  and  $R^{10}$  show hydrogen or a hydrocarbon group of the carbon numbers 1-20. What has  $m$  pieces,  $n$  pieces,  $l$  pieces,  $k$   $R^6$ ,  $n$  pieces, and  $p$  respectively the same  $R^7$  may differ.  $X$  shows a divalent substituent of the carbon numbers 0-10 which contain only C, H, N, O, S, and halogen as a comprising element.



(m)=2, n)=0, l, q)>=1, and p are an integer of 0-5, and  $3 \leq (m+n+l+p) \leq 20$  among a formula (7), and  $R^6, R^7, R^8$ , and X are the same as a formula (6).

[Claim 8](A) A hardenability constituent whose aforementioned (B) ingredient an organic compound which contains at least one carbon-carbon double bond in a molecule, and an organic system hardening agent which has (B) hydroxyl group are used as an essential ingredient, and a hardening agent given in any 1 paragraph of the 1st paragraph of a claim – the 7th paragraph.

[Claim 9](C) A hardenability constituent given in the 8th paragraph of a claim containing a hydroxyl group catalyst further.

[Claim 10](A) An organic compound which contains at least one carbon-carbon double bond in a molecule. And a fizz resin composition whose aforementioned (B) ingredient a compound which has an organic system hardening agent (D) foaming agent and/or an OH radical which have (B) hydroxyl group is used as an essential ingredient, and is an organic system hardening agent.

Line 10-11A paragraph on a claim that has any one or more solvents or inner structures as a molecular skeleton, or a **fizz resin composition given in the 11th paragraph.**  
[Claim 14]A **fizz resin composition given in any 1 paragraph of the 10-13th paragraphs of a claim,** wherein the number of carbon-carbon double bonds of an organic compound of the aforementioned (A) ingredient is an average of two or more per molecule.  
[Claim 15]A **fizz resin composition given in any 1 paragraph of the 10-14th paragraphs of a claim** whose foaming agents of the aforementioned (D) ingredient are compounds chosen from hydrocarbon, hydrochlorofluorocarbon, or hydrofluorocarbon, or those mixtures.

[Claim 16] A fizz resin composition given in any 1 paragraph of the 10-15th paragraphs of a claim, wherein a compound which has an OH radical of the aforementioned (D) ingredient consists of one or more sorts in alcohol, carboxylic acid, and water.

[Claim 17] Foam produced by making a fizz resin composition of a statement react to any 1 paragraph of the 10-16th paragraphs of a claim.

[Claim 18] A manufacturing method of foam characterized for a fizz resin composition given in any 1 paragraph of the 10-16th paragraphs of a claim by ordinary temperature or making it react under low-temperature heating comparatively, and carrying out foam curing.

[Translation done.]